Mixed-Metal Oxo Clusters Structurally Derived from Ti₆O₄(OR)₈(OOCR')₈

Christine Artner,[a] Ayse Koyun,[a] Matthias Czakler,[a] and Ulrich Schubert*[a]

Keywords: Cluster compounds / Bimetallic compounds / Titanium / Chain structures / Carboxylate ligands

The mixed-metal oxo clusters FeTi₅O₄(OiPr)(OMc)₁₀ (OMc = methacrylate), Zn₂Ti₄O₄(OiPr)₂(OMc)₁₆, Cd₂Ti₃O₃(OMc)₂(OMe)₁₀, [Ca₂Ti₄O₄(OMe)₁₀(OH)O]₉, and [Sr₂Ti₄O₄(OMc)₁₀(HOMc)₂]ₙ were obtained from the reaction of titanium alkoxides with the corresponding metal acetates and methacrylic acid. Their structures are derived from Ti clusters with the composition Ti₆O₄(OR)₈(OOCR')₈. The Ca and Sr derivatives consist of chains of condensed clusters.

Introduction

Oxo clusters of the general composition TiₐO₇(OR)₈(OOCR')₈ are obtained when titanium alkoxides, Ti(OR)₄, are treated with more than one molar equivalent of a carboxylic acid.[1] The carboxylic acid not only provides carboxylate ligands but also acts as an in situ water source through esterification with the eliminated alcohol. The outcome of the reaction depends, among others, on the groups R and R’ as well as the Ti(OR)₄/R/COOH ratio. Many oxo clusters have been isolated with different degrees of condensation (a:b ratio), different degrees of substitution (a:d ratio), different proportions of residual OR groups (a:c ratio), and, as a consequence, different structures. One of the more prominent structure types is Ti₆O₄(OR)₈(OOCR')₈, which was obtained for several R/R’ combinations.[2,3] An example, with R = iPr and OOCR = OMc (Ti6) (HOMc = methacrylic acid), is shown in Figure 1.

In this article, we describe the structures of mixed-metal oxo clusters that are derived from that of Ti₆O₄(OR)₈(OOCR')₈. The variability of this structural motif shows that this is a robust structure that not only tolerates variations of R and R’, but also that of the metal polyhedra of which it is composed.

Mixed-metal clusters have been prepared by addition of carboxylic acids to metal alkoxide mixtures.[4] We have previously shown that use of metal acetates as one of the components is a good alternative, because they are readily avail-

---

[a] Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, 1060 Vienna, Austria
E-mail: Ulrich.Schubert@tuwien.ac.at
http://www.imc.tuwien.ac.at

© 2014 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
DOI:10.1002/ejic.201402499

Eur. J. Inorg. Chem. 2014, 5008–5014
Wiley Online Library
5008
able and easy to handle. The mixed-metal clusters described in this article were therefore prepared from Ti(OrPr)₄ and metal acetates as precursors. We chose a selection of divalent metals (M) with different ionic radii and different preferred coordination numbers to find out how these parameters influence the structures of the clusters, keeping in mind that the charges of the metal as well as the total number of coordination sites must be balanced by the ligands to get a stable cluster.

\[
\text{Ti(O} \text{OrPr)}_4 + M(OAc) + \text{MeOH} \rightarrow \text{Ti}_{1-}M(O\text{OrPr})_2(\text{OMc})_2(O\text{Ac})_2 + R\text{COO}M\text{Pr} + \ldots
\]

In previous work on carboxylate-substituted metal oxo clusters, we were initially using methacrylic acid to get clusters that can be polymerized subsequently to obtain hybrid materials. It turned out that methacrylic acid is particularly well suited to the production of crystalline clusters. This may be owing to sterics reasons and/or a suitable balance of substitution versus esterification reaction rates. We therefore used methacrylic acid in this work as well, although in this case no subsequent polymerizations were intended.

Results and Discussion

Although several clusters of the composition Ti₆O₄(OR)₈⁻(OOCR)₄⁻ are known with various R/R' combinations, we prepared the derivative with R = Pr and OOCR = OMc (Ti₆) (Figure 1) for better comparison of the structural parameters with that of the mixed-metal clusters reported in this article. The centrosymmetric Ti₆O₄ core is formed by two Ti₃(μ₂-O) units, which are connected through two μ₃-oxygen atoms. An alternative description of the structure is that of a Ti₆O₄ ring of four corner-sharing octahedra to which two Ti octahedra (called “outer Ti” in the following) are condensed through shared edges. Balancing of charges and coordination numbers is achieved by two bridging OPr ligands (connecting the two edge-sharing octahedra), eight bridging carboxylate ligands and six terminal OPr ligands.

Treatment of Fe(OAc)₂ and Ti(OOrPr)₄ (2 equiv.) with methacrylic acid (17 equiv.) resulted in reddish-brown crystals of Fe₃Ti₄O₈(OrPr)₂(OMc)₁₀ (FeTi₅) (Figure 2). The cluster core of FeTi₅ is isostructural to that of Ti₆. Although attachment of the “outer” Ti octahedra is the same as in Ti₆, the four Ti atoms of the Ti₆O₄ ring are partly replaced by Fe atoms owing to the nearly identical ionic radii of Ti⁴⁺ (0.605 Å) and low-spin Fe²⁺ in an octahedral coordination (0.61 Å). Distinction between these two elements in the crystal structure is not straightforward. The Ti/Fe₁ site (corresponding to Ti2 in Ti₆) was refined with an occupancy for Fe of 34% and that of Ti/Fe₂ (corresponding to Ti1 in Ti₆) with 16%. To prove incorporation of both metals, the crystals were washed with dry n-heptane and their metal content was checked with energy-dispersive X-ray spectroscopy (EDX), through which both Fe and Ti were found in the crystals.

FeTi₅ needs two negative ligands less than Ti₆ because of the lower charge of Fe²⁺, but the total number of coordination sites to be occupied by the ligands is the same because all metal atoms in both Ti₆ and FeTi₅ are octahedrally coordinated. Thus, the two terminal OPr groups O12 (on Ti2) and O14 (on Ti3) in Ti₆, which are nearly parallel to each other are replaced by one bridging OMc ligand in FeTi₅ (O9 and O10) (compare Figures 1 and 2). As a consequence of this substitution, the coordination octahedra in FeTi₅ are slightly tilted relative to Ti₆. This results, among other things, in slightly different distances between the metal centers (3.4215, 3.4917, and 3.0466 Å in FeTi₅ compared with 3.3783, 3.5862, and 3.1062 Å in Ti₆ for analogous distances).

Reaction of Zn(OAc)₂ with Ti(OOrPr)₄ and methacrylic acid in different molar ratios afforded the centrosymmetric cluster Zn₃Ti₄O₈(OrPr)₂(OMc)₁₀ (Zn₂Ti₄, Figure 3). The structure of this cluster is again structurally related to that of Ti₆, with the two outer Ti octahedra being replaced by Zn tetrahedra. Contrary to Ti₆ and FeTi₅, in which the outer Ti octahedra share an edge with one of the octahedra of the Ti₆O₄ unit, the Zn tetrahedra share a corner with two Ti octahedra. The μ₃-oxygen (O1) is slightly shifted towards the titanium atoms [Zn₁–O1 1.975(1) Å, Ti₁–O1 1.871(1) and 1.923(1) Å], which results in a widening of the Ti₁–O₁–Ti₂ angle to 136.01(7)° compared to 128.00(5)° in Ti₆ and 127.1(1)° in FeTi₅.

Zn₂Ti₄ needs four negative ligands less than Ti₆ (and two less than FeTi₅) to compensate the metal charges because two Ti⁴⁺ are replaced by two Zn⁺. The total number of coordination sites to be occupied by the ligands is reduced by four relative to Ti₆ and FeTi₅ (replacement of two octahedra by two tetrahedra). Compared to Ti₆, four terminal OPr ligands are missing (the ones at Ti3 and Ti3*...
in Ti6), and the O\textsubscript{Pr} ligands bridging Ti1 and Ti3 in Ti6 are replaced by a bridging O\textsubscript{Me} ligand in Zn2Ti4.

In addition to the \(\mu_1\)-oxygen atom (O1), the Zn atom is connected to both neighboring Ti atoms through bridging O\textsubscript{Me} ligands, two to Ti1 and one to Ti2. The oxygen atoms of these three O\textsubscript{Me} ligands, together with the \(\mu_1\)-oxygen atom, form a tetrahedron around Zn. The Zn–O distances of the O\textsubscript{Me} ligands vary only slightly between 1.940(2) and 1.959(2) Å and are not much shorter than the Zn–O1 distances (1.957(2) Å). The Zn–O distances (HO–Zn) vary only slightly between 1.921(14) and 1.931(14) Å.

Figure 3. Molecular structure of Zn\(_2\)Ti\(_4\)(\(\mu_1\)-O\(_2\))(\(\mu_3\)-O\(_2\))(O\textsubscript{Pr})$_2$ (Zn2Ti4). Hydrogen atoms are omitted for clarity. Selected bond lengths and angles: Zn1–Ti1 3.147(4), Zn1–Ti2 3.270(4), Ti1–Ti2 3.365(2), Zn1–O1 1.974(13), Ti1–O1 1.871(13), Ti1–O2 1.755(13), Ti2–O1 1.921(14), Ti2–O2 1.878(13), Ti2–O(13) 1.782(14), Zn1–O3 1.946(2), Zn1–O7 1.959(2), Zn1–O10 2.038(3), Ti1–O13 1.986(2), Ti1–O14 2.227(2), Cd1–O6 2.256(2), Cd1–O8 2.260(2), Cd2–O10 2.279(3), Cd2–O12 2.228(3) Å; Zn1–O1–Ti1 109.80(7), Zn1–O1–Ti2 114.05(6), Ti1–O1–Ti2 136.01(7)°.

Selected bond lengths and angles: Zn1–Ti1 3.1470(4), Zn1–Ti2 3.2701(4), Ti1–Ti2 3.3652(5), Zn1–O1 1.9747(13), Ti1–O1 1.8712(13), Ti1–O2 1.7550(13), Ti2–O1 1.9231(14), Ti2–O2 1.8784(13), Ti2–O(13) 1.7821(14), Zn1–O3 1.946(2), Zn1–O7 1.959(2), Zn1–O10 2.0383(15), Ti1–O13 1.986(2), Ti1–O14 2.227(2), Cd1–O6 2.256(2), Cd1–O8 2.260(2), Cd2–O10 2.279(3), Cd2–O12 2.228(3) Å; Zn1–O1–Ti1 109.80(7), Zn1–O1–Ti2 114.05(6), Ti1–O1–Ti2 136.01(7)°.

The very short Ti–O1 bond length of 1.698(2) Å is due to the coordinated ROH in the trans position. All the metal atoms in both Ti6 and Cd4Ti2 are octahedrally coordinated. The total positive charge of the metals, however, is +24 in Ti6 but only +16 in Cd4Ti2. This means that a smaller number of (monoanionic) ligands must satisfy the coordination requirements of the metals. In addition to the ligands discussed before, coordination of the Cd\(_4\) core must be completed by two O\textsubscript{Me} and two O\textsubscript{Ac} ligands. This can only be achieved if each of the carboxylate ligands is tridentate. Thus, one oxygen atom (O2) of the remaining O\textsubscript{Me} ligands bridges C d1 and Cd1', and the second (O3) is coordinated to Cd2. The acetate ligands are bridging-chelating [O4 bridges Cd1 and Cd2; O4 and O5 chelate Cd2]. The coordination octahedron of Cd2 is much more distorted than that of Cd1 due to the chelating carboxylate. Whereas the cis O–Cd1–O angles of Cd1 are between 75.0(1) and 97.9(1)°, those of Cd2 are between 55.50(8) and 109.49(9)°.

Figure 4. Molecular structure of Cd3Ti1(\(\mu_1\)-O2)(\(\mu_1\)-OAc)2(\(\mu_3\)-OMe)3(3-OAc)2(3-OMe)2(3-O)2(OCHCF3)4(OAc)4. Selected bond lengths and angles: Ti1–Cd1 3.4499(9), Ti1–Cd2 3.4521(9), Cd1–Cd2 3.8904(8), Ti1–O1 1.698(2), Cd1–O1 2.262(2), Cd2–O1 2.267(2), Cd1–O2 2.260(2), Cd1–O2 2.355(2), Cd1–O4 2.232(2), Cd2–O3 2.267(3), Cd2–O4 2.336(2), Cd2–O5 2.369(2), Ti1–O7 2.012(2), Ti1–O9 1.997(2), Ti1–O11 1.977(2), Ti1–O13 1.986(2), Ti1–O14 2.227(2), Cd1–O6 2.256(2), Cd1–O8 2.260(2), Cd2–O10 2.279(3), Cd2–O12 2.228(3) Å; Cd1–O1–Cd2 118.40(9), Cd1–O1–Ti1 120.55(11), Cd2–O1–Ti1 120.36(11)°.

The very short Ti–O1 bond length of 1.698(2) Å is due to the coordinated ROH in the trans position. All the metal atoms in both Ti6 and Cd4Ti2 are octahedrally coordinated. The total positive charge of the metals, however, is +24 in Ti6 but only +16 in Cd4Ti2. This means that a smaller number of (monoanionic) ligands must satisfy the coordination requirements of the metals. In addition to the ligands discussed before, coordination of the Cd\(_4\) core must be completed by two O\textsubscript{Me} and two O\textsubscript{Ac} ligands. This can only be achieved if each of the carboxylate ligands is tridentate. Thus, one oxygen atom (O2) of the remaining O\textsubscript{Me} ligands bridges C d1 and Cd1', and the second (O3) is coordinated to Cd2. The acetate ligands are bridging-chelating [O4 bridges Cd1 and Cd2; O4 and O5 chelate Cd2]. The coordination octahedron of Cd2 is much more distorted than that of Cd1 due to the chelating carboxylate. Whereas the cis O–Cd1–O angles of Cd1 are between 75.0(1) and 97.9(1)°, those of Cd2 are between 55.50(8) and 109.49(9)°.

The \(\mu_1\)-OMe and the chelating/bridging acetate cause a shorter distance between the symmetry-related Cd1 atoms than the corresponding Ti atoms in Ti4 or Zn2Ti4. The distance between Cd1 and Cd1' [3.6618(8) Å] is comparable to that of Cd1–Cd2 [3.8904(8) Å] and Cd1–Cd2' [3.9525(8) Å]. However, the symmetry-related Cd2 atoms are moved further apart [Cd2–Cd2' 6.9358(14) Å].

Another carboxylate-substituted Cd/Ti oxo cluster reported in the literature, Cd3Ti1O4(OCH2CH2NMe2)4(OCCF3)4(OAc)4, is also based on four interconnected Cd polyhedra. In this case, however, the Cd4 unit is capped by two condensed Ti octahedra on both sides.

Reaction of an equimolar mixture of Ca(OAc)\(_2\) and Ti(O\textsubscript{Pr})\(_4\) with a tenfold excess amount of methacrylic acid resulted in centrosymmetric Cd3Ti1O4(OAc)2(O\textsubscript{Me})10-(HO\textsubscript{Pr})\(_2\) (Cd4Ti2, Figure 4). The structure of this cluster can again be related to that of Ti6, but there are more profound changes. (i) In contrast to the structures discussed before, the four Ti atoms in the center are replaced by Cd atoms, (ii) acetate groups [originating from the Cd(OAc)\(_2\) precursor] were incorporated in the structure, (iii) two Cd atoms are bridged across the Cd4O4 ring, and (iv) the structure contains no \(\mu_2\)-oxygen atoms, only the \(\mu_3\)-O units are retained.

The titanium atoms are symmetrically connected to the central Cd4 unit through four bridging O\textsubscript{Me} ligands each (two to each neighboring Cd atom) as well as a \(\mu_1\)-O atom connecting Cd1, Cd2, and Ti1. Ti1 is approximately equidistant to both Cd [Ti1–Cd1 3.4499(9) Å, Ti1–Cd2 3.4521(9) Å]. The octahedral coordination of Ti1 is completed by a coordinated isopropyl alcohol. The alcoholic proton was identified in the electron density map, and the long Ti1–O14 distance [2.2186(3) Å] proves additionally that this is a coordinated alcohol rather than a O\textsubscript{Pr} group.
to that in Zn2Ti4. Owing to the lower charge of Ca2+ and its higher coordination number, the clusters are condensed to endless parallel chains of Ca2Ti4 units (Figure 5), contrary to the molecular clusters discussed before. The Ca2Ti4 repeating units are connected through a chelating-bridging acetate ligand. The acetate ligand is chelating Ca1, while one of its oxygen atoms (O3) is bridging Ca1 and Ti1, and the other (O4) Ca1 and Ca1'. The Ca1–O4 bond length [2.660(2) Å] is much longer than that of Ca1’–O4 [2.292(2) Å].

The proton of the methacrylic acid is hydrogen bonded to a non-coordinated butanol, and the proton of the butanol in turn to an oxygen atom (O7) of one of the bridging OMc ligands. The bridging HOMc moves the Ca atoms closer to each other [Ca1–Ca2 3.7089(8) Å] and also affects the linking carboxylate group. The Ca–O bond lengths of the chelating ligands at Ca1 are now equal [Ca1–O3 2.560(2), Ca1–O4 2.510(2), Ca1–O5 2.361(2), Ca1–O7 2.317(2), Ca1–O9 2.342(2)], as well as the Ti–O bond lengths of these ligands [1.935(2)–1.931(2) Å].

When the molar ratio of Ti(OBu)4/Pr(OAc)2 in the precursor mixture was increased from 1:1 to 2:1, while keeping the proportion of methacrylic acid per metal constant, a variation of the structure of Ca2Ti4 was observed. The Ca2–Ti4 bond lengths of the OMC ligands differ only slightly [2.317(2) and 2.361(2) Å], as well as the Ti–O bond lengths and angles: Ca1–Ca1 3.5083(6), Ca1–Ti1 3.5606(7), Ca1–Ti2 3.6737(7), Ca1–O1 2.510(2), Ti1–O1 1.931(2), Ti1–O2 1.745(2), Ti2–O1 1.774(2), Ti2–O2 1.875(2), Ca1–O3 2.560(2), Ca1–O4 2.510(2), Ca1’–O4 2.360(2), Ti1–O3 2.101(2), Ca1–O5 2.362(2), Ca1–O7 2.358(2), Ti1–O6 1.935(2), Ti2–O8 1.967(2), Ti2–O10 1.957(2), Ca1–O15 2.489(2), Ca2–O15 2.812(2), Ti1–O11 2.025(2), Ti1–O13 2.045(2), Ti2–O12 2.127(2) Å; Ca1–O1–Ti1 106.22(8), Ca1–O1–Ti2 117.52(9), Ti1–O1–Ti2 136.12(10)°.

In addition to the chelating-bridging acetate ligand and the μ3-oxygen, Ca1 is also connected to Ti1 through a μ3-oxygen atom (O3) is bridging Ca1 and Ti1, and the other (O4) Ca1 and Ca1'. The Ca1–O4 bond length [2.660(2) Å] is much longer than that of Ca1’–O4 [2.292(2) Å].
gands, one oxygen atom of the COO group bridges the two Sr atoms and the other oxygen atom binds to Ti1 (or Ti3, respectively).

\[
\text{Figure 7. Structure of } [\text{Sr}_2\text{Ti}_4(\mu_3-\text{O})_2(\mu_2-\text{OMc})_2(\mu_2-\text{OMc})_2(\mu_3-\text{HOMc})_2]_2 \text{ (SrTi4).}
\]

| Bond Lengths (Å) | Bond Lengths (Å) |
|------------------|------------------|
| Sr1–Ti1 3.6312(4) | Sr1–O1 2.581(2)  |
| Sr1–Ti2 3.7280(4) | Sr1–O15 2.632(2) |
| Ti1–Ti2 3.3691(5)| Sr1–O13 2.946(2) |
| Sr1–Ti2 2.877(2)  | Sr1–O14 2.558(2)  |
| Sr2–O4 2.598(4)| Ti1–O13 2.107(2)  |
| Sr2–O5 2.705(2)  | Ti1–O3 2.017(2)  |
| Sr1–O7 2.632(2)  | Ti1–O2 1.883(2)  |
| Sr1–O8 2.556(2)| Ti2–O1 1.884(2)  |
| Sr2–O4 2.598(4)| Ti2–O2 1.777(2)  |
| Sr2–O4A 2.438(13) | Ti2–O2 1.777(2)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |
| Sr1–O13 2.946(2) | Sr2–O4 2.598(4)  |
| Sr2–O4A 2.438(13) | Sr2–O4 2.598(4)  |

**Conclusion**

The structure of all the clusters described in this article can be derived from that of Ti6. The general structure is retained when part of the Ti atoms is replaced by two-valent atoms (Fe2+, Zn2+, Cd2+, Ca2+, Sr2+), but the lower charge of the second metal renders modification of the ligand sphere necessary. Depending on the preferred coordination number of the two-valent atoms, this adaptation occurs differently. In addition to different coordination of the negatively charged ligands, completion of the coordination sphere is also possible by coordination of neutral ligands (ROH, MeO), as observed in Cd4Ti2, Ca2Ti4a, or Sr2Ti4.

Fe2+ and Ti4+ have similar bonding characteristics with oxygen and the ionic radii are almost equal (0.61 and 0.605 Å), hence the four inner Ti4+ sites are partly replaced by Fe2+ atoms (FeTi5). In contrast, the ionic radius of Cd2+ is much bigger (0.95 Å). This results in a different arrangement of the coordination octahedra in Cd4Ti2, namely, replacement of the inner Ti atoms by Cd. The lower charge is compensated by a different coordination behavior of the smaller number of ligands.

Although the size of Zn2+ is the same as that of Fe2+ and Ti4+ (0.61 Å), it usually exhibits tetrahedral coordination. Hence a partial substitution of the Ti atoms is not possible. In Zn2Ti4, the two outer Ti octahedra are replaced by Zn tetrahedra, with corresponding adjustment of the connecting ligands.

Ca2+ and Sr2+ ions are much bigger, have higher coordination numbers (seven-coordinated Ca2+ 2.00 Å, eight-coordinate Sr2+ 2.17 Å, ten-coordinated Sr2+ 2.33 Å), and the bonds are less directed. In the Ca and Sr compounds, the outer Ti octahedra are substituted with Ca or Sr polyhedra. Different to FeTi5, Zn2Ti4, and Cd4Ti2 where molecular clusters were obtained, Ca2Ti4, Ca2Ti4a, and Sr2Ti4 form chains of condensed clusters in the crystal lattice. This is enabled by the higher coordination of Ca2+ and Sr2+.

**Experimental Section**

**General**

All experiments were carried out under an argon atmosphere using standard Schlenk techniques. Ti(OBU)4, Fe(OAc)3, and Sr(OAc)2 were obtained from Aldrich, Ti(OPr)4 from ABCR, Ca(OAc)2·H2O and Zn(OAc)2·H2O from Fluka, and Cd(OAc)2·H2O from Merck. Water-free metal acetates were obtained by drying under vacuum at 130 °C overnight (verified by IR spectroscopy). All solvents used for NMR spectroscopy (Euriso-top) were degassed prior to use and stored over molecular sieves.

**General Preparative Procedure: Ti(OPr)4**, the corresponding water-free metal acetate and an excess amount of methacrylic acid were mixed. No solvent was added unless otherwise stated. The mixture was left standing in a closed vessel until crystals were formed.

FeTi2O2(10Pr)2(OMc)10 (FeTi6): The red-brown solution of Fe(OAc)2 (1 mmol, 0.174 g), Ti(OPr)4 (2 mmol, 0.568 g), and methacrylic acid (17 mmol, 1.44 g) was stirred for one week and then filtered. Reddish-brown crystals were obtained after two weeks, yield 0.120 g (41% rel. Ti).

Zn2Ti2O2(10Pr)2(OMc)10 (Zn2Ti4): Ti(OPr)4 (1 mmol, 0.284 g), dry Zn(OAc)2 (1 mmol, 0.183 g), and methacrylic acid (10 mmol, 0.861 g) were mixed at room temperature. After addition of methacrylic acid the mixture immediately turned orange. Dry CH2Cl2 (1.5 mL) was added to the mixture. After 1 week orange crystals were isolated from the mother liquid, yield (after washing with dry n-heptane): 0.256 g (77% rel. to Ti).

1H NMR (CDCl3, 250 MHz, 1H): δ = 1.22 (m, 12 H, CHMe), 1.81–2.11 (m, 30 H, =CHMe), 4.52 (sep, 2 H, CHMe), 5.35–5.68 (m, 10 H, =CH3), 5.98–6.43 (m, 10 H, =CH2).
Table 1. Crystal data, data collection parameters, and refinement details.[a]

| Compound     | Ti6          | FeTi5        | Zn2Ti4       | Cd4Ti2       |
|--------------|--------------|--------------|--------------|--------------|
| Empirical formula | C_{6}H_{10}O_{36}Ti_{6} | C_{5}H_{10}Fe_{0.5}O_{14}Ti_{2.5} | C_{4}H_{6}O_{36}Ti_{4}Zn_{2} | C_{5}H_{7}O_{28}Ti_{2} |
| Space group  | P2\text{I}/c  | P2\text{I}/m  | P2\text{I}/m  | P2\text{I}/c  |
| a [Å]        | 11.5503(4)   | 12.0904(10)  | 13.1321(5)   | 21.026(4)    |
| b [Å]        | 18.9581(5)   | 11.1928(9)   | 16.7388(7)   | 22.290(4)    |
| c [Å]        | 17.0246(5)   | 24.1989(19)  | 22.8051(5)   | 15.173(3)    |
| α [°]        | 90           | 90           | 81.340(2)    | 90           |
| β [°]        | 105.1810(10) | 93.803(3)    | 13.1321(5)   | 110.224(5)   |
| γ [°]        | 90           | 90           | 83.9400(11)  | 90           |
| V [Å³]       | 359.71(19)   | 1.425        | 1.425        | 0.661        |
| Z            | 2            | 4            | 1            | 4            |
| D_{calc} [g/cm³] | 1.389      | 1.558        | 1.558        | 1.379        |
| μ [mm⁻¹]     | 0.710        | 0.859        | 1.425        | 1.661        |
| Mean. indep., obsd. reflections [I > 2σ(I)] | 103239, 14090, 10638 | 9521, 8702, 6080 | 18055, 18055, 13178 | 122456, 10180, 8084 |
| R_{int}      | 0.0523       | 0.0439       | 0.0817       | 0.031        |
| η_{max}      | 33.50        | 28.85        | 37.02        | 30.52        |
| R^{(2)} > 2σ(F^2), S | 0.0361, 0.889, 1.032 | 0.0721, 0.1880, 1.119 | 0.0476, 0.1160, 1.000 | 0.0367, 0.0839, 1.224 |
| Parameters   | 418          | 399          | 359          | 391          |

Table 2. Crystal data, data collection parameters, and refinement details.[a]

| Compound     | Ca2Ti4       | Ca2Ti4a      | Sr2Ti4       |
|--------------|--------------|--------------|--------------|
| Empirical formula | C_{5}H_{2}Ca_{4}O_{31}Ti_{2} | C_{5}H_{2}Ca_{5}O_{31}Ti_{4} | C_{5}H_{2}Ca_{5}O_{31}Sr_{2}Ti_{4} |
| Crystal system | orthorhombic | orthorhombic | orthorhombic |
| Space group  | Pccn         | Pccn         | Pccn         |
| a [Å]        | 20.4104(7)   | 13.9656(6)   | 12.7300(4)   |
| b [Å]        | 23.1828(9)   | 15.3582(7)   | 13.4769(4)   |
| c [Å]        | 12.5984(4)   | 16.7388(7)   | 22.8051(5)   |
| α [°]        | 90           | 81.340(2)    | 83.9400(11)  |
| β [°]        | 90           | 83.406(2)    | 83.5000(11)  |
| γ [°]        | 90           | 75.256(2)    | 63.5000(11)  |
| V [Å³]       | 5961.2(4)    | 3421.4(3)    | 3452.6(2)    |
| Z            | 8            | 2            | 2            |
| D_{calc} [g/cm³] | 1.454      | 1.447        | 1.562        |
| μ [mm⁻¹]     | 0.77         | 0.684        | 2.06         |
| Crystal size [mm] | 0.45 × 0.40 × 0.22 | 0.29 × 0.23 × 0.19 | 0.20 × 0.18 × 0.15 |
| T_{min}, T_{max} | 0.6321, 0.7472 | 0.6636, 0.7455 | 0.5171, 0.7465 |
| Mean. indep., obsd. reflections [I > 2σ(I)] | 257146, 14564, 9971 | 101946, 15413, 10380 | 117417, 21081, 14895 |
| R_{int}      | 0.0692       | 0.071        | 0.0598       |
| η_{max}      | 36.74        | 27.44        | 30.58        |
| R^{(2)} > 2σ(F^2), S | 0.0645, 0.1799, 1.183 | 0.0940, 0.1208, 1.062 | 0.0388, 0.885, 1.202 |
| Parameters   | 358          | 850          | 877          |
| Weighting scheme[a] | x = 0.0517, y = 13.5390 | x = 0.0564, y = 1.8169 | x = 0.0344, y = 2.5320 |

[a] ω = 1/[σ(2(F^2)) + (xP)^2 + yP], in which P = (F^2 + 2P^2)/3.
The same compound was obtained when dry Ca(OAc)$_2$ (2 mmol, 0.363 g) and Ti(OBu)$_4$ (2 mmol, 0.702 g) were treated with methacrylic acid (18 mmol, 1.55 g). Colorless crystals were obtained after filtration of the reaction solution.

$[\text{Ca}_2\text{Ti}_4\text{O}_4(\text{OAc})(\text{OMc})_{11}(\text{HOMc})\cdot\text{BuOH}]_n$ (Ca2Ti4a): Dry Ca(OAc)$_2$ (1 mmol, 0.182 g) and Ti(OiPr)$_4$ (2 mmol, 0.568 g) were treated with methacrylic acid (13.5 mmol, 1.162 g). After two weeks colorless crystals formed, in addition to much of a white insoluble and amorphous precipitate.

$[\text{Sr}_2\text{Ti}_4\text{O}_4(\text{OMc})_{12}(\text{HOMc})_2]_n$ (Sr2Ti4): Sr(OAc)$_2$ (1 mmol, 0.411 g) and Ti(OBu)$_4$ (1 mmol, 0.351 g) were treated with methacrylic acid (12 mmol, 1.03 g). Small amounts of precipitate were formed after three days in the originally clear solution. After 6 weeks a big colorless crystal was formed.

X-ray Structure Analyses: Crystallographic data were collected on a Bruker AXS SMART APEX II four-circle diffractometer with $\kappa$-geometry at 100 K using Mo-$K\alpha$ ($\lambda = 0.71073$ 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. SAINT PLUS software (Bruker Analytical X-ray Instruments, 2007) was used to integrate the frames. Symmetry was then checked with the program PLATON.[10]

The structures were solved by charge flipping (JANA2006). Refinement was performed by the full-matrix least-squares method based on $F^2$ (SHELXL97) 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 Tables 1 and 2.

CCDC-1005662 (for Ti6), -1005663 (for FeTi5), -1005664 (for Zn2Ti4), -1005665 (for Cd4Ti2), -1005666 (for Ca2Ti4), -1005667 (for Ca2Ti4a), and -1005668 (for Sr2Ti4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Fonds zur Förderung der wissenschaftlichen Forschung (FWF), Austria (project P22536). The authors thank the X-ray center of Vienna University of Technology for technical support.

[1] U. Schubert, J. Mater. Chem. 2005, 15, 3701–3715.
[2] B. Moraru, N. Hüsing, G. Kickelbick, U. Schubert, P. Fratzl, H. Peterlik, Chem. Mater. 2002, 14, 2732–2740.
[3] I. Gautier-Luneau, A. Mosset, J. Galy, Z. Kristallogr. 1987, 180, 83–95; U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich, C. Chau, Chem. Mater. 1992, 4, 291–295; P. S. Ammala, S. R. Batton, C. M. Kepert, L. Spiccia, A. M. Van der Bergen, B. O. West, Inorg. Chem. Acta 2003, 353, 75–81; S. Doeuff, Y. Dromzee, F. Taulelle, C. Sanchez, Inorg. Chem. 1989, 28, 4439–4445; I. Laaziz, A. Larbot, C. Guizard, J. Durand, L. Cot, J. Joffre, Acta Crystallogr., Sect. C 1990, 46, 2332–2334; G. Kickelbick, D. Holzinger, C. Brick, G. Trimmel, E. Moons, Chem. Mater. 2002, 14, 4382–4389; Y. Gao, F. R. Kogler, H. Peterlik, U. Schubert, J. Mater. Chem. 2006, 16, 3268–3276; P. Heinz, M. Puchberger, M. Bendova, S. O. Baumann, U. Schubert, Dalton Trans. 2010, 39, 7640–7644.
[4] B. Moraru, G. Kickelbick, U. Schubert, Eur. J. Inorg. Chem. 2001, 1295–1301; M. Jupa, G. Kickelbick, U. Schubert, Eur. J. Inorg. Chem. 2004, 1835–1839.
[5] C. Artner, M. Czakler, U. Schubert, Chem. Eur. J. 2014, 20, 493–498.
[6] U. Schubert, J. Sol-Gel Sci. Technol. 2003, 26, 47–55.
[7] U. Schubert, Chem. Mater. 2001, 13, 3487–3494.
[8] R. D. Shannon, Acta Crystallogr., Sect. A 1976, 32, 751–767.
[9] S. Abu Bakar, S. Tjahjannil Hussain, M. Mazhar, New J. Chem. 2012, 36, 1844–1851.
[10] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Determination, University of Göttingen, Germany, 1997.