Ion-Size-Dependent Formation of Mixed Titanium/Lanthanide Oxo Clusters

Christine Artner,[a] Stefan Kronister,[a] Matthias Czakler,[a] and Ulrich Schubert*[a]

Dedicated to Professor Gerhard Roewer on the occasion of his 75th birthday

Keywords: Cluster compounds / Lanthanides / Titanium / Carboxylate ligands

The mixed-metal oxo clusters LnTi3O6(OMc)12(OiPr)2 (Ln = La, Ce; OMc = methacrylate), Ln3Ti3O2(OMc)14(HOPr) (Ln = La, Ce, Nd, Sm) and Ln3Ti4O4(OMc)14(HOMc)2 (Ln = Sm, Eu, Gd, Ho) have been synthesized from titanium isopropoxide, the corresponding lanthanide acetate and methacrylic acid. The type of cluster obtained strongly depends on the size of the lanthanide ion.

Introduction

We have recently described mixed Ti/M oxo clusters with divalent metals M (Ca, Sr, Zn, Cd). These clusters have a basic hexanuclear structure that varies according to the size and coordination number of the M2+ ions.[1] In another series of Ti/M oxo clusters with divalent metals (M = Sr, Pb), crown ether type structures were obtained.[2] The clusters were prepared by the reaction of Ti(OR)4 with the corresponding metal acetate [M(OAc)2] and methacrylic acid (McOH). The carboxylic acid not only provides carboxylate ligands [Equation (1a)], but also acts as an in situ source of water through its esterification with the eliminated alcohol [Equation (1b)]. Methacrylic acid was initially used to obtain carboxylate-substituted metal oxo clusters that can subsequently polymerize to yield hybrid materials.[3] It turned out, however, that methacrylic acid is particularly well suited to obtain crystalline clusters. We therefore used methacrylic acid in this work as well, although no subsequent polymerizations were intended.

\[
\text{Ti(OiPr)4} + \text{McOH} \rightarrow \text{Ti(OiPr)4} + \text{PrOH} \quad (1a)
\]

\[
\text{iPrOH} + \text{McOH} \rightarrow \text{MeOPr} + \text{H}_2\text{O} \quad (1b)
\]

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

The charges on the metal atoms as well as the total number of coordination sites must be balanced by the ligands to obtain a stable cluster.[4] For this reason, clusters of different compositions are expected if the metal charge is varied. Carboxylate-substituted TiM oxo clusters with trivalent metals are only known for Y. In previous work, three Y/Ti clusters of the general composition \(\text{Er}_2\text{Ti}_4\text{O}_9\text{OMc}_4\text{HOMc}_2\) (Y2Ti4).\([5]\] Because the variance of the ion size of trivalent rare-earth ions is much smaller than that of the divalent metals mentioned above, much more detailed information on the dependence of ion size of a specific cluster structure can be expected. This is the topic of this article. The mixed Ti/Ln clusters were prepared according to [Equation (1c)].

\[
\text{Ti(OiPr)4} + \text{Ln(OAc)}_3 + \text{H}_2\text{O} \rightarrow \text{Ti}_{2}\text{Ln}_3\text{O}_4\text{(OiPr)}_4\text{(OMc)}_6 + ... \quad (1c)
\]

Size-dependent structural changes have been found, for example, for Ln(OMes)3 (OMes = 2,4,6-trimethylphenolate), with the dinuclear species Ln2(OMes)6(thf)4 with two bridging OMes ligands observed for the larger ions La and Nd, whereas the mononuclear compounds Ln(OMes)3(thf)3 were found for Sm, Tb, Er, Yb and Y.[6] The metal atoms are six-coordinate in both structures.

A few Ln/Ti oxo/alkoxo clusters are known, but none of them contains ligands other than oxo and alkoxo groups. The structure of K3Eu2TiO2(OtBu)11(OMes/OH)(OtBuOH) is based on a K3Eu2O octahedron capped by a K3TiO tetrahedron on the K3 face,[7] and the metal atoms in
Sm$_2$TiO(OiPr)$_4$[8] and (Tb$_{0.9}$Er$_{0.1}$)$_2$TiO(OiPr)$_4$[9] form a trigonal bipyramid with an encapsulated $\mu_3$-oxygen atom.

Although the work reported here involves only structural issues, the mixed Ln/Ti clusters could be interesting precursors for mixed-oxide materials[10]

Results and Discussion

In the course of this work we found that Y2Ti4[5] is also formed when Y(OAc)$_3$ is used as the Y precursor instead of Y(OCH$_3$CH$_3$OMe)$_3$. Isomorphous and isostructural clusters were obtained from lanthanide acetates that have Ln$^{3+}$ ion radii similar to that of Y$^{3+}$ (1.109 Å). Centrosymmetric clusters La$_2$Ti$_6$O$_4$(OMe)$_{12}$Ho1(HOMe)$_2$ (Ln2Ti4, Figure 1) were thus synthesized from Ln(OAc)$_3$ (Ln = Sm, Eu, Gd, Ho), Ti(OiPr)$_4$, and methacrylic acid with the ratio of Ln(OAc)$_3$/Ti(OiPr)$_4$ ranging from 2:1 to 1:2. The bond lengths and angles of Sm2Ti4, Eu2Ti4, Gd2Ti4 and Ho2Ti4 (as well as Y2Ti4) are almost the same; therefore, only those of Eu2Ti4 are discussed exemplarily. The Ln atom in the Ln2Ti4 structures shows positional disorder with 66:34 occupancy, Eu1A is shifted relative to the Eu1 position by 0.247(7) Å.

![Figure 1. Molecular structure of Eu2Ti4(OiPr)$_4$](Image)

The basic structural motif of Ln2Ti4 is a zigzag chain of two central [LnO$_8$] dodecahedra and two terminal [TiO$_6$] octahedra (Ti1) that share edges. Two additional [TiO$_6$] octahedra (Ti2) are condensed onto this Ln2Ti2 core in Ln2Ti6, the same central structural element, namely a zigzag chain of two central [LnO$_8$] dodecahedra and two terminal [TiO$_6$] octahedra (Ti1) that share edges. Two other OMC ligands are necessary to balance the charges on the Ln$_3$Ti$_4$O$_4$ core, and 28 coordination sites must still be occupied.

The Ti–O distances of the oxygen atom that connects Ti2 to the main chain [Ti2–O2 1.733(3) Å] are in the same range as that of Ti1–O1 [1.718(2) Å], whereas Ti1–O2 is significantly lengthened [2.022(2) Å].

In the case of Ln2Ti4, the total metal charge is +22, and the number of coordination sites is 40, assuming six-coordinate Ti atoms and eight-coordinate Ln atoms. Thus, 14 monoanionic ligands are necessary to balance the charges of the Ln$_3$Ti$_4$O$_4$ core, and 28 coordination sites must still be occupied. This requirement would be met if all OMC ligands in Ln2Ti4 were bidentate. Apparently this is not possible for steric reasons, and two OMC ligands coordinate only in an $\eta^1$ manner; to occupy all the available coordination sites two neutral MeOH ligands are additionally coordinated to the same Ti atom (Ti2). Both interact with each other through a strong hydrogen bond [O16…O18 2.454(8) Å in Eu2Ti4]. Because the Ti2–O15 distance is significantly longer than that of Ti2–O17 [Ti2–O15 2.140(2), Ti2–O17 1.974(3) Å], it is likely that the hydrogen atom is closer to O16. We pointed out earlier that the combination of an $\eta^1$ and a neutral proton-donating ligand connected through a hydrogen bond (Scheme 1) is structurally equivalent to a monoanionic bidentate ligand.[11] Due to the octahedral coordination of Ti, chelating carboxylate ligands are extremely rare. Such coordination would cause too large a distortion of the Ti coordination sphere.

![Scheme 1. $\eta^1$-Carboxylate ligand stabilized by a coordinated RCOOH (left, as in Ln2Ti4) or R’OH molecule (right, as in Ln2Ti6).](Image)

All the other OMC ligands in Ln2Ti4 bridge two metal atoms each. Ln1 and Ti1 as well as Ti1 and Ti2 are bridged by one OMC ligand, while Ln1 and Ti2 as well as Ln1 and Ti1$^+$ are bridged by two OMC ligands.

Clusters with the composition Ln$_2$Ti$_6$O$_4$(OMe)$_{18}$ (HOiPr)$_2$ (Ln2Ti6) were obtained (Ln = Nd, Ce, La) with a larger Ln$^{3+}$ ion radius (Figure 2). This type of cluster was also obtained for Ln = Sm (Sm2Ti6) when the reaction mixture with a Ti/Sm precursor ratio of 2:1 was heated at 80 °C.

The centrosymmetric clusters La2Ti6, Ce2Ti6, Nd2Ti6 and Sm2Ti6 are again isomorphous and isostructural; the structural parameters will therefore only be discussed for La2Ti6.

In this cluster, the Ln atoms also show positional disorder with a 85:15 occupancy and an La1–La1A distance of 0.27(3) Å.

The structures of Ln2Ti6 and Ln2Ti4 are based on the same central structural element, namely a zigzag chain of two central [LnO$_8$] dodecahedra and two terminal [TiO$_6$] octahedra (Ti1) that share edges. Four additional [TiO$_6$] octahedra are condensed onto this Ln$_3$Ti$_2$ core in Ln2Ti6, however, instead of the two in Ln2Ti4. Two of the four [TiO$_6$] octahedra (Ti2) share edges with the [LnO$_8$] dodecahedra, and the other two (Ti3) share a corner with the polyhedra of Ln and one of the Ti atoms.
The metal atoms are connected through six μ₁-oxo oxygen atoms, one (O1) connecting Ln, Ln' and Ti1, the second Ln, Ti1 and Ti2, and the third Ln, Ti2 and Ti3. The La–O3 distance is relatively long (3.045(3) Å compared with La1–O1 2.538(3), La1–O1’ 2.552(3), La1–O2 2.526(3), La1–O3 3.045(3), La1–O4 2.447(4), La1–O6 2.482(4), La1–O8 2.496(4), La1–O10 2.545(4), La1–O12 2.458(4), Ti1–O1 1.705(3), Ti1–O2 1.987(3), Ti1–O5 2.004(3), Ti1–O7 1.977(3), Ti1–O9 1.990(3), Ti1–O14 2.185(3), Ti2–O2 1.743(3), Ti2–O3 1.976(3), Ti2–O11 1.915(4), Ti2–O15 1.974(3), Ti2–O16 2.023(3), Ti2–O18 2.101(3), Ti3–O3 1.742(3), Ti3–O13 1.944(4), Ti3–O17 2.010(4), Ti3–O19 2.011(4), Ti3–O20 1.924(4), Ti3–O22 2.158(4); La1–O1 2.6410(18), La1–O2 2.4793(17), La1–O3 2.6228(18), La1–O4 2.5455(18), La1–O6 2.447(2), La1–O8 2.5447(19), La1–O10 2.558(2), La1–O12 2.533(2), La1–O14 2.548(2), Ti1–O1 1.9688(18), Ti1–O5 1.927(2), Ti1–O7 1.977(2), Ti1–O16 2.038(2), Ti1–O18 2.051(2), Ti2–O1 1.7904(18), Ti2–O2 1.8249(18), Ti2–O3 1.8226(19), Ti2–O9 1.981(2), Ti2–O17 2.056(2), Ti2–O19 2.019(2), Ti2–O20 2.0826(19), Ti3–O3 1.7786(18), Ti3–O11 1.975(2), Ti3–O12 2.084(2), Ti3–O22 2.041(2), Ti3–O24 2.035(2), Ti4–O3 1.9702(19), Ti4–O13 1.925(2), Ti4–O15 1.938(2), Ti4–O23 2.029(2), Ti4–O25 2.046(2), Ti4–O27 1.774(2); O1–La1–O2 60.33(6), O2–La1–O3 60.40(6)*, O1–La1–Ti1 131.54(15), La1–O2–Ti1 99.27(12), La1–O2–Ti2 116.61(15), Ti1–O2–Ti2 142.62(17), La1–O3–Ti3 130.38(16), Ti2–O3–Ti3 130.7(2).

Contrary to the structures of Ln2Ti4 and Ln2Ti6, the cluster core of LnTi4 contains only one Ln atom, which is surrounded by a semicircle of four [TiO₂] octahedra (Figure 3). The La distances to the two terminal, edge-sharing Ti atoms Ti1 and Ti4 are much longer than those to the central, face-sharing Ti atoms [La1–Ti1 4.128(6), La1–Ti4 4.053(6), La1–Ti2 3.449(5), La1–Ti3 3.4571(7) Å]. Each of the three μ₁-O atoms link two [TiO₂] octahedra to the central Ln atom. All the metal atoms and core oxygen atoms are nearly coplanar. Although the Ti–O bond lengths of the two central Ti atoms Ti2 and Ti3 are the shortest
in the structure [Ti2–O1 1.790(2), Ti2–O2 1.825(2), Ti3–O2 1.841(2), Ti3–O3 1.779(2) Å], those of Ti1 and Ti4 are significantly longer [Ti1–O1 1.969(2), Ti4–O3 1.970(2) Å]. The same applies for La, with La1–O2 [2.479(2) Å] about 0.2 Å shorter than La1–O1 [2.641(2) Å] and La1–O3 [2.623(2) Å].

The Ln atom is also connected to the Ti atoms through OMc bridges. This results in an overall coordination number of nine for Ln. The coordination polyhedron can be described as a square-faced monocapped antiprism (SAPRS-9).[12] The terminal Ti atoms Ti1 and Ti4 are additionally coordinated by four bridging OMc ligands, two of which connect Ti1 and Ti4 to the Ln atom and the other two to the central Ti atoms Ti2 and Ti3. The coordination sphere of Ti1 and Ti4 is completed by a terminal OPr ligand. Ti2 and Ti3 are additionally connected to each other by an OMc bridge and to Ln by one bridging OMc ligand each. The latter ligands are arranged on opposite sides of the plane of the cluster core, almost perpendicular to the plane. The bond lengths are in the same range as before [La1–O8 2.545(2), La1–O10 2.558(2), Ti2–O9 1.981(2), Ti3–O11 1.975(2) Å]. The structure can also be derived from the previously described clusters Sr2Ti6O14(OMc)16 and Pb2Ti3O8(OMc)18(BuOH)2, in which the two central Sr/Pb atoms are surrounded by a ring of eight Ti atoms. LnTi4 can be seen as half of the Sr/Ti or Pb/Ti cluster. Alternatively, it may be considered half of the Ln2Ti6 cluster core, in which an additional [TiO6] octahedron is condensed to the Ln atom instead of there being a “dimerization” of the LnTi3 unit by condensation of two [LnO6] polyhedra.

Conclusions

The cluster structures described in this article show a clear correlation with the ionic radii of the trivalent metal atom (see Table 1). Clusters with the composition Ln2Ti4O3(OMc)14(HOMc)2 (Ln2Ti4) were formed with the larger ions (ion radii 1.08–1.16 Å for Pr)2(OAc)2(OMc)16 and Nd(OAc)3·H2O, were obtained from Aldrich. Ti(OPr)4, Ho(OAc)3·H2O and Nd(OAc)3·H2O were purchased from ABCR. The acetates were dried in a vacuum chamber at 130 °C overnight, and the removal of water was monitored by IR spectroscopy. All solvents used for NMR spectroscopy (Eurisotop) were degassed prior to use and stored over molecular sieves. 1H and 13C NMR spectra in solution were recorded with a Bruker Avance 250 spectrometer [250.13 MHz (1H), 62.86 MHz (13C)] equipped with a 5 mm inverse-broadband probe head and a z-gradient unit. IR spectra were recorded with a Bruker Tensor 27 spectrometer under ambient conditions with 32 scans at a resolution of 4 cm−1 on a diamond ATR unit.

X-ray Crystallography: Crystallographic data were collected with a Bruker AXS SMART APEX II four-circle diffractometer with ω geometry at 100 K by using Mo-Kα (λ = 0.71073 Å) radiation. The data were corrected for polarization and Lorentzian 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. The asymmetry was then verified by using the PLATON program.[13] The structures were solved by charge flipping (JANA2006). Refinement was performed by the full-matrix least-squares method based on F2 (SHELXL97)[13] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bound to carbon atoms were inserted at calculated positions and refined by using a riding model. Hydrogen atoms bound to oxygen atoms were identified on the difference electron density map, and the O–H bond lengths were then fixed.

Table 1. Comparison of the cluster type depending on coordination characteristics (c.n. = coordination number).

| Metal    | c.n. | Ion radius [Å] | M–O [Å] | Cluster core |
|----------|------|----------------|---------|--------------|
| La3+    | 9    | 1.216          | 2.45–2.64 | LaTi4O3    |
| Ce3+    | 9    | 1.196          | 2.42–2.62 | CeTi4O3    |
| La3+    | 8    | 1.16           | 2.46–2.55 | La2Ti6O6   |
| Ce3+    | 8    | 1.143          | 2.41–2.53 | Ce2Ti6O6   |
| Nd3+    | 8    | 1.109          | 2.38–2.51 | Nd2Ti6O6   |
| Sm3+    | 8    | 1.079          | 2.31–2.57 | Sm2Ti6O6   |
| Eu3+    | 8    | 1.066          | 2.32–2.49 | Eu2Ti4O4   |
| Gd3+    | 8    | 1.053          | 2.27–2.51 | Gd2Ti4O4   |
| Ho3+    | 8    | 1.015          | 2.28–2.52 | Ho2Ti4O4   |
| Y3+     | 8    | 1.019          | 2.28–2.55 | Y2Ti4O4    |
General Synthetic Procedure: Ti(OPr)4, the corresponding water-free metal acetate and an excess of methacrylic acid were mixed. No solvent was added. The mixture was left to stand in a closed vessel until crystals had formed.

$$Y_2Ti_4O_7(OMc)_4(HOMc)_2 (Y_2Ti_4):$$
Y(OAc)3 (1 mmol, 0.266 g) was mixed with Ti(OPr)4 (2 mmol, 0.568 g) and methacrylic acid (13.5 mmol, 1.162 g). The solution was stirred for 1 d. Orange crystals were isolated after 1 week. Yield: 0.51 g (57% based on Y). IR: $\tilde{\nu} = 2979$ (w), 2927 (w), 1697 (w), 1643 (w), 1563 (s), 1545 (m), 1385 (s), 1368 (s), 1232 (s), 1007 (m), 938 (m), 852 (w), 826 (w), 760 (s), 654 (m) cm$^{-1}$.

$$Eu_2Ti_4O_7(OMc)_4(HOMc)_2 (Eu_2Ti_4):$$
Eu(OAc)$_3$ (1 mmol, 0.329 g) was mixed with Ti(OPr)4 (2 mmol, 0.568 g) and methacrylic acid (13.5 mmol, 1.162 g). The solution was stirred for 1 d. Colourless crystals of Eu2Ti4 were isolated after 1 week. Yield: 0.779 g (81% based on Eu). The cluster was also obtained when Eu(OAc)$_3$ (1 mmol, 0.329 g) was mixed with Ti(OPr)4 (2 mmol, 0.568 g) and heated at about 80 °C for 2 h, followed by cooling to room temperature and addition of methacrylic acid (13.5 mmol, 1.162 g). IR: $\tilde{\nu} = 2979$ (w), 2927 (w), 1697 (w), 1643 (w), 1560 (s), 1454 (m), 1384 (s), 1367 (s), 1232 (s), 1006 (m), 937 (m), 852 (w), 825 (s), 758 (m), 601 (s) cm$^{-1}$.

$$Ho_2Ti_4O_7(OMc)_4(HOMc)_2 (Ho_2Ti_4):$$
Ho(OAc)$_3$ (1 mmol, 0.342 g) was mixed with Ti(OPr)4 (2 mmol, 0.568 g) and methacrylic acid (13.5 mmol, 1.162 g). The solution was stirred for 1 d. Orange crystals were isolated after 1 week. Yield: 0.756g (78% based on Ho). The cluster was also obtained with Ho/Ti ratios of 1:1 and 2:1 in the precursor mixture. IR: $\tilde{\nu} = 2979$ (w), 2927 (w), 2929 (w), 1698 (w), 1643 (w), 1564 (s), 1546 (m), 1384 (s), 1367 (s), 1232 (s), 1129 (w), 1006 (m), 937 (m), 852 (w), 825 (s), 758 (m), 601 (s) cm$^{-1}$.

Table 2. Crystal data, data collection parameters and refinement details of Ln2Ti4.

| Ln Industry | Sm2Ti4 | Eu2Ti4 | Gd2Ti4 | Ho2Ti4 |
|-----------------|--------|--------|--------|--------|
| Empirical formula | C$_{64}$H$_{82}$Sm$_2$O$_{36}$Ti$_4$ | C$_{64}$H$_{82}$Eu$_2$O$_{36}$Ti$_4$ | C$_{64}$H$_{82}$Gd$_2$O$_{36}$Ti$_4$ | C$_{64}$H$_{82}$Ho$_2$O$_{36}$Ti$_4$ |
| M$_r$ | 1919.6 | 1922.82 | 1933.4 | 1948.76 |
| Crystal system | triclinic | triclinic | triclinic | tetraclinic |
| Space group | P$\bar{1}$ | P$\bar{1}$ | P$\bar{1}$ | P$\bar{1}$ |
| $a$ [Å] | 11.377(2) | 11.3836(8) | 11.395(3) | 11.3819(14) |
| $b$ [Å] | 12.406(2) | 12.3936(8) | 12.403(4) | 12.3656(14) |
| $c$ [Å] | 14.521(3) | 14.5215(10) | 14.436(4) | 14.470(2) |
| $\alpha^\circ$ | 81.779(5) | 81.777(5) | 81.777(5) | 81.777(5) |
| $\beta^\circ$ | 82.168(5) | 82.168(5) | 82.168(5) | 82.168(5) |
| $\gamma^\circ$ | 77.779(5) | 77.673(2) | 77.591(5) | 77.239(2) |
| $V$ [Å$^3$] | 1979.36 | 1977.52 | 1967.4(10) | 1962.1(4) |
| $D_c$ [Mg m$^{-3}$] | 1.609 | 1.615 | 1.632 | 1.649 |
| $\mu$ [mm$^{-1}$] | 1.930 | 2.033 | 2.135 | 2.467 |
| Crystal size [mm] | 0.25×0.24×0.14 | 0.33×0.30×0.29 | 0.34×0.29×0.20 | 0.36×0.29×0.20 |
| $T_{min}$, $T_{max}$ | 0.6442, 0.7739 | 0.5535, 0.5902 | 0.5306, 0.6748 | 0.6129, 0.6651 |
| No. measd., indep., obsd. refl. | 71616, 9215, 7690 | 87054, 12723, 9772 | 91177, 11236, 10189 | 86970, 11125, 9310 |
| $I > 2\sigma (I)$ | 0.0435 | 0.0495 | 0.0634 | 0.0583 |
| $\theta_{max}$ [°] | 27.71 | 31.18 | 29.82 | 29.74 |
| $R(F^2 > 2\sigma (F^2))$, $wR(F^2)$, $S$ | 0.041, 0.087, 1.147 | 0.036, 0.096, 1.100 | 0.042, 0.107, 1.119 | 0.035, 0.098, 1.186 |
| Weighting scheme | $x = 0.0178$, $y = 11.8006$, $z = 0.3344$ | $x = 2.9260$ | $x = 0.0528$, $y = 6.0150$ | $x = 0.0277$, $y = 6.4784$ |
| $\delta_{max}$, $\delta_{max}$ [Å$^2$] | 3.549, –1.416 | 2.573, –1.077 | 1.904, –1.705 | 3.804, –1.640 |

[a] $\omega = 1/[\sigma(F_i^o)^2 + (xP_i^2 + yP_i)]$, in which $P = (F_o^2 + 2F_e^2)/3$. 

Eur. J. Inorg. Chem. 2014, 5596–5602
Table 3. Crystal data, data collection parameters and refinement details of Ln2Ti6.

| Ln2Ti6 | Ce2Ti6 | Nd2Ti6 | Sm2Ti6 |
|--------|--------|--------|--------|
| Empirical formula | C24H106La2O44Ti6 | C24H106Ce2O44Ti6 | C24H106Nd2O44Ti6 | C24H106Sm2O44Ti6 |
| \(M_r\) | 2312.76 | 2315.19 | 2323.44 | 2335.68 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | \(P2_1/n\) | \(P2_1/n\) | \(P2_1/n\) | \(P2_1/n\) |
| \(a\) [Å] | 13.2380(10) | 13.2605(4) | 13.2949(8) | 13.3506(7) |
| \(b\) [Å] | 25.401(2) | 25.3631(8) | 25.2718(16) | 25.1832(13) |
| \(c\) [Å] | 16.1311(3) | 16.1410(5) | 16.1480(10) | 16.2144(8) |
| \(\beta\) [°] | 113.48(3) | 113.5940(10) | 113.9472(2) | 113.897(2) |
| \(V\) [Å³] | 4975.0(7) | 4974.8(3) | 4961.9(5) | 4984.1(4) |
| \(Z\) | 2 | 2 | 2 | 2 |
| \(\rho\) [Mg m⁻³] | 1.544 | 1.437 | 1.550 | 1.556 |
| \(\rho\) [mm⁻³] | 1.381 | 1.437 | 1.570 | 1.700 |
| Crystal size [mm] | 0.30 × 0.27 × 0.22 | 0.35 × 0.22 × 0.20 | 0.38 × 0.28 × 0.23 | 0.45 × 0.38 × 0.30 |
| \(T_{\text{min}}\) | 0.6821, 0.7509 | 0.6331, 0.7620 | 0.5869, 0.7141 | 0.5151, 0.6296 |
| No. measd., indep., obsd. refl. \([I > 2\sigma(I)]\) | 217332, 239975, 33064 | 253922, 27295, 3604 | 315033, 20740, 14016 | 318904, 20940, 17821 |
| \(R_{\text{int}}\) | 0.035 | 0.064 | 0.0479 | 0.0429 |
| \(\theta_{\text{int}}, [°]\) | 31.14 | 32.32 | 34.48 | 34.75 |
| \(R^2 > 2\sigma(F)\), \(\sigma(R(F))^2\), S | 0.062, 0.140, 1.33 | 0.045, 0.114, 1.21 | 0.068, 0.168, 1.25 | 0.045, 0.100, 1.31 |
| Weighting scheme\(^{[a]}\) | \(x = 0.0134, y = 19.2502\) | \(x = 0.0331, y = 18.4502\) | \(x = 0.0337, y = 19.5161\) | \(x = 0.0184, y = 11.8747\) |
| \(\delta_{\text{max}} / \delta_{\text{min}}\) [Å⁻³] | 1.752, -1.350 | 1.374, -1.352 | 2.207, -1.815 | 2.255, -1.540 |

\(^{[a]}\) \(\omega = 1/\sqrt{(\sigma(F)^2) + (xP)^2 + yP}^2\), in which \(P = (F^2 + 2F^2)/3\).

Table 4. Crystal data, data collection parameters and refinement details of LnTi4.

| LnTi4 | CeTi4 |
|-------|-------|
| Empirical formula | Ce₂H₂O₆La₂O₂₇Ti₄ | Ce₂H₂O₆CeO₂₇Ti₄ |
| \(M_r\) | 1432.56 | 1433.66 |
| Crystal system | triclinic | triclinic |
| Space group | \(P\) | \(P\) |
| \(a\) [Å] | 11.83(3) | 11.79(3) |
| \(b\) [Å] | 12.84(5) | 12.91(3) |
| \(c\) [Å] | 0.36 × 0.34 × 0.30 | 0.35 × 0.28 × 0.23 |
| \(\rho\) [Mg m⁻³] | 1.517 | 1.506 |
| \(\rho\) [mm⁻³] | 1.233 | 1.267 |
| Crystal size [mm] | 0.36 × 0.34 × 0.30 | 0.35 × 0.28 × 0.23 |
| \(T_{\text{min}}\) | 0.6841, 0.7464 | 0.6773, 0.7459 |
| No. measd., indep., obsd. refl. \([I > 2\sigma(I)]\) | 217332, 36907, 30664 | 210874, 34198, 28928 |
| \(R_{\text{int}}\) | 0.034 | 0.051 |
| \(\theta_{\text{int}}, [°]\) | 30.15 | 29.68 |
| \(R^2 > 2\sigma(F)\), \(\sigma(R(F))^2\), S | 0.048, 0.011, 1.159 | 0.039, 0.087, 1.10 |
| Weighting scheme\(^{[a]}\) | \(x = 0.0308, y = 10.2792\) | \(x = 0.0258, y = 7.7323\) |
| \(\delta_{\text{max}} / \delta_{\text{min}}\) [Å⁻³] | 0.972, -1.086 | 1.164, -0.916 |

\(^{[a]}\) \(\omega = 1/\sqrt{(\sigma(F)^2) + (xP)^2 + yP}^2\), in which \(P = (F^2 + 2F^2)/3\).
172.5 (COO, OMc) ppm. IR: ν = 2975 (w), 2927 (w), 1698 (w), 1645 (m), 1577 (s), 1516 (m), 1454 (s), 1414 (s), 1385 (s), 1365 (s), 1235 (m), 1162 (w), 1123 (m), 936 (m), 857 (m), 825 (m), 741 (m), 659 (m) cm⁻¹.

Nd₂Ti₆O₆(OMc)₁₈(HOᵢPr)₂ (Nd₂Ti₆): Nd(OAc)₃ (1 mmol, 0.321 g) was mixed with Ti(OᵢPr)₄ (2 mmol, 0.568 g) and methacrylic acid (13.5 mmol, 1.162 g). The solution was stirred for 1 d and filtered through a syringe filter. Orange crystals were isolated after 1 week. Yield: 0.293 g (76% based on Ti). IR: ν = 2976 (w), 2927 (w), 1697 (w), 1643 (w), 1532 (s), 1541 (s), 1454 (m), 1363 (s), 1329 (s), 1230 (s), 1122 (w), 1007 (w), 939 (m), 849 (w), 828 (m), 808 (m), 739 (s), 657 (m) cm⁻¹.

Sm₂Ti₆O₆(OMc)₁₈(HOᵢPr)₂ (Sm₂Ti₆): Sm(OAc)₃ (1 mmol, 0.327 g) was mixed with Ti(OᵢPr)₄ (2 mmol, 0.568 g) and heated at 80 °C for 2 h. The mixture was cooled to room temperature, and then methacrylic acid (13.5 mmol, 1.162 g) was added. The solution was stirred for 16 h. Orange crystals were isolated after 2 weeks. Yield: 0.251 g (43% based on Sm). ¹H NMR (CD₂Cl₂, 250 MHz): δ = 1.19–1.34 (m, 12 H, CH₃, OᵢPr), 1.69 (s, 3 H, CH₃, OMc), 1.76–2.36 (m, 51 H, CH₃, OMc), 4.60–4.80 (m, 2 H, CH, OᵢPr), 5.34–5.92 (m, 18 H, =CH₂, OMc), 6.31–6.80 (m, 18 H, =CH₂, OMC) ppm. IR: ν = 2973 (w), 2926 (w), 1697 (w), 1641 (w), 1594 (w), 1527 (s), 1454 (s), 1403 (s), 1389 (s), 1367 (s), 1241 (m), 1206 (w), 1047 (w), 1024 (w), 932 (m), 852 (w), 832 (m), 692 (m), 659 (w) cm⁻¹.

LaTi₄O₃(OᵢPr)₂(OMc)₁₁ (LaTi₄): La(OAc)₃ (1 mmol, 0.316 g) was mixed with Ti(OᵢPr)₄ (2 mmol, 0.568 g) and methacrylic acid (13.5 mmol, 1.162 g). The solution was stirred for 1 d. Dark yellow crystals were isolated after 2 weeks. Yield: 0.567 g (79% based on La). ¹H NMR (CD₂Cl₂, 250 MHz): δ = 1.19–1.28 (m, 12 H, CH₃, OᵢPr), 1.62–2.08 (m, 33 H, CH₃, OMC), 4.02 (sept, 2 H, CH, OᵢPr), 5.29–5.68 (m, 11 H, =CH₂, OMC), 5.90–6.13 (m, 11 H, =CH₂, OMC) ppm. IR: ν = 2978 (w), 2928 (w), 1680 (w), 1640 (w), 1542 (s), 1453 (m), 1403 (s), 1385 (s), 1366 (m), 1326 (m), 1231 (m), 1208 (w), 1053 (w), 1006 (w), 936 (m), 863 (w), 829 (m), 759 (w), 675 (m), 656 (m) cm⁻¹.

CeTi₄O₃(OᵢPr)₂(OMc)₁₁ (CeTi₄): Ce(OAc)₃ (1 mmol, 0.317 g) was mixed with Ti(OᵢPr)₄ (2 mmol, 0.568 g) and methacrylic acid (28 mmol, 2.712 g). The solution was stirred for 1 d. Orange crystals were isolated after 2 weeks. Yield: 1.06 g (74% rel. Ce).

Acknowledgments

Special thanks to Anja Wiesner for performing the Nd experiments. This work was supported by the Fonds zur Förderung der wissenschaftlichen Forschung (FWF), Austria (project P22915). The authors thank the X-ray Center of Vienna University of Technology for its support.

[1] C. Artner, A. Koyun, M. Czakler, U. Schubert, Eur. J. Inorg. Chem. 2014, 5008–5014.
[2] C. Artner, M. Czakler, U. Schubert, Chem. Eur. J. 2014, 20, 493–498.
[3] U. Schubert, Chem. Mater. 2001, 13, 3487–3494.
[4] U. Schubert, J. Sol-Gel Sci. Technol. 2003, 26, 47–55.
[5] M. Jupa, G. Kickelbick, U. Schubert, Eur. J. Inorg. Chem. 2004, 1835–1839.
[6] G. B. Deacon, J. P. Junk, G. J. Moxey, Chem. Asian J. 2009, 4, 1717–1728.
[7] E. Berger, G. Westin, J. Sol-Gel Sci. Technol. 2010, 53, 681–688.
[8] S. Daniele, L. G. Hubert-Pfalzgraf, J.-C. Daran, S. Halut, Polyhedron 1994, 13, 927–932.
[9] M. Moustiakimov, M. Kritikos, G. Westin, Acta Crystallogr., Sect. C 1998, 54, 29–31.
[10] For a recent relevant review article, see: L. John, P. Sobota, Acc. Chem. Res. 2014, 47, 470–481.
[11] E. R. Kogler, M. Jupa, M. Puchberger, U. Schubert, J. Mater. Chem. 2004, 14, 3133–3138.
[12] R. M. Hartshorn, E. Hey-Hawkins, R. Kalio, G. J. Leigh, Pure Appl. Chem. 2007, 79, 1779–1799.
[13] A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7–13.

Received: July 16, 2014
Published Online: October 6, 2014