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

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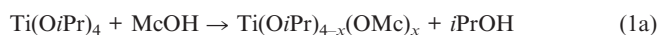*Dedicated to Professor Gerhard Roewer on the occasion of his 75th birthday*

The mixed-metal oxo clusters $LnTi_4O_3(OiPr)_2(OMc)_{11}$ (Ln = La, Ce; OMc = methacrylate), $Ln_2Ti_6O_6(OMc)_{18}(HOiPr)$ (Ln = La, Ce, Nd, Sm) and $Ln_2Ti_4O_4(OMc)_{14}(HOMc)_2$ (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 M^{2+} 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 obtaining crystalline clusters. We therefore used methacrylic acid in this work as well, although no subsequent polymerizations were intended.

$$Ti(OiPr)_4 + McOH \rightarrow Ti(OiPr)_{4-x}(OMc)_x + iPrOH \qquad (1a)$$

$$iPrOH + McOH \rightarrow McOiPr + H_2O \qquad (1b)$$

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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 $Ti_4Y_2O_4(OMc)_{12}X_2L_2$ (X = η^1-OMc or OCH_2CH_2OMe; L = $MeOCH_2CH_2OH$ or McOH) were obtained upon treating $Ti(OiPr)_4$ and $Y(OCH_2CH_2OMe)_3$ with methacrylic acid, among them $Y_2Ti_4O_4(OMc)_{14}(HOMc)_2$ (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)].

$$Ti(OiPr)_{4-x}(OMc)_x + Ln(OAc)_3 + H_2O \rightarrow$$
$$Ti_aLn_bO_c(OiPr)_d(OMc)_e + ... \qquad (1c)$$
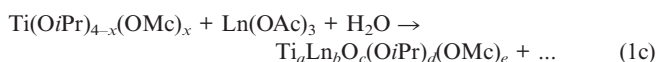
Size-dependent structural changes have been found, for example, for $Ln(OMes)_3$ (OMes = 2,4,6-trimethylphenolate), with the dinuclear species $Ln_2(OMes)_6(thf)_4$ with two bridging OMes ligands observed for the larger ions La and Nd, whereas the mononuclear compounds $Ln(OMes)_3(thf)_3$ were found 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 $K_3Eu_3TiO_2(OtBu)_{11}(OMe/OH)(tBuOH)$ is based on a K_3Eu_3O octahedron capped by a K_3TiO tetrahedron on the K_3 face,[7] and the metal atoms in

$Sm_4TiO(OiPr)_{14}$[8] and $(Tb_{0.9}Er_{0.1})_4TiO(OiPr)_{14}$[9] form a trigonal bipyramid with an encapsulated μ_5-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 $Y(OCH_3CH_3OMe)_3$. 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 $Ln_2Ti_4O_4(OMc)_{14}(HOMc)_2$ (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.
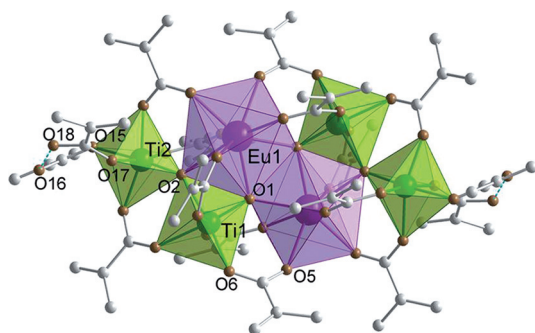

Figure 1. Molecular structure of $Eu_2Ti_4(\mu_3\text{-}O)_4(\mu_2\text{-}OMc)_{12}(\eta^1\text{-}OMc)_2(\eta^1\text{-}HOMc)_2$ (Eu2Ti4). Hydrogen atoms have been omitted for clarity. Blue dashed lines indicate hydrogen bonds. Selected bond lengths [Å] and angles [°]: Eu1–O1 2.319(3), Eu1–O1' 2.457(4), Eu1–O2 2.491(3), Eu1–O3 2.368(3), Eu1–O5 2.464(3), Eu1–O7 2.330(4), Eu1–O9 2.341(4), Eu1–O11 2.382(4), Ti1–O1 1.718(2), Ti1–O2 2.022(2), Ti1–O4 2.019(2), Ti1–O6 1.958(2), Ti1–O8 1.992(2), Ti1–O13 2.128(2), Ti2–O2 1.730(2), Ti2–O10 1.987(3), Ti2–O12 1.981(3), Ti2–O14 1.991(3), Ti2–O15 2.140(2), Ti2–O17 1.974(3); Eu1–O1–Eu1' 111.06(11), Eu1–O1–Ti1 108.87(12), Eu1–O1–Ti1' 133.59(12), Eu1–O2–Ti1 93.46(10), Eu1–O2–Ti2 126.19(12), Ti1–O2–Ti2 137.75(12).

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 the main chain at both ends of the zigzag chain through shared corners. Thus, Ti1 is bonded to two μ_3-oxygen atoms, with Ln, Ln' and Ti1 (' denotes symmetry-related atoms) are connected through O1 and Ln, Ti1 and Ti2 connected through O2. The oxygen atom O1 in Eu2Ti4 is slightly unsymmetrically located between the two Eu atoms [Eu1–O1 2.319(3), Eu1'–O1 2.457(4) Å]; the distance of Eu1 to the other μ_3-oxygen atom (O2) is only slightly lengthened [Eu1–O2 2.491(3) Å].

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 $Ln_2Ti_4O_4$ 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 η^1 manner; to occupy all the available coordination sites two neutral McOH 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)], it is likely that the hydrogen atom is closer to O16. We pointed out earlier that the combination of an η^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.
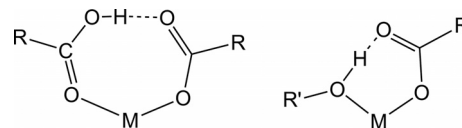
Scheme 1. η^1-Carboxylate ligand stabilized by a coordinated RCOOH (left, as in Ln2Ti4) or R'OH molecule (right, as in Ln2Ti6).

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 $Ln_2Ti_6O_6(OMc)_{18}(HOiPr)_2$ (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_2Ti_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.
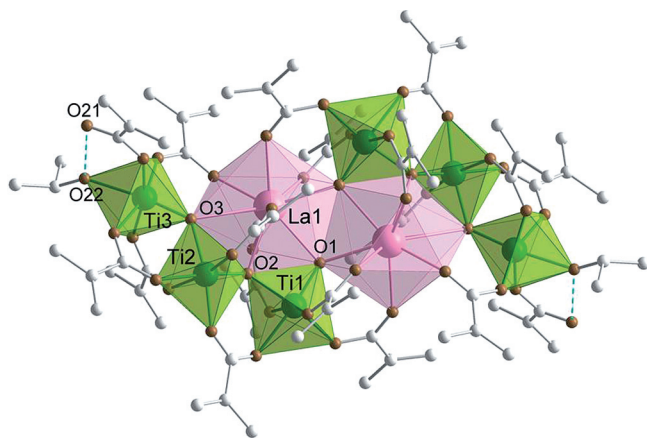
Figure 2. Molecular structure of La₂Ti₆(μ₃-O)₆(μ₂-OMc)₁₈-(HO*i*Pr)₂ (La2Ti6). Hydrogen have been omitted for clarity. Blue dashelines indicate hydrogen bonds. Selected bond lengths [Å] and angles [°]: La1–O1 2.538(3), La1–O1′ 2.552(3), La1–O2 2.526(3), La1–O3 3.045(3), La1–O4 2.447(4), La1–O6 2.482(4), 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 1.954(3), 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–La1 112.93(12), La1–O1–Ti1 107.50(14), La1–O1–Ti1′ 131.54(15), La1–O2–Ti1 99.27(12), La1–O2–Ti2 116.61(15), Ti1–O2–Ti2 142.62(17), La1–O3–Ti2 90.89(11), La1–O3–Ti3 130.38(16), Ti2–O3–Ti3 130.7(2).

The metal atoms are connected through six μ₃-oxygen atoms, one (O1) connecting Ln, Ln′ and Ti1, the second Ln, Ti1 and Ti2, and the third Ln, Ti2 and Ti3. The La1–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) Å], and therefore it can be debated whether O3 is a μ₃-oxygen atom with a very long La–O distance (and nine-coordinate Ln) or a μ₂-oxygen atom with a short La–O contact (and eight-coordinate Ln). The Ti–O bond lengths also differ widely. Each Ti atom has one very short bond to a core oxygen atom [Ti1–O1 1.705(3), Ti2–O2 1.743(3), Ti3–O3 1.742(3) Å], but the Ti1–O2 and Ti2–O3 bonds are more than 0.2 Å longer [Ti1–O2 1.987(3). Ti2–O3 1.976(3) Å].

The same calculation as above shows that 18 mononegative bidentate ligands are required to balance the 30 positive charges of the metal atoms and the 36 remaining coordination sites of the Ln₂Ti₆O₆ core (again assuming six-coordinate Ti atoms and eight-coordinate Ln atoms). As discussed above, and for the same reason, two of the OMc ligands (at Ti3 and Ti3′) are only η¹-coordinated and are stabilized by a hydrogen-bonded neutral ligand [O···O 2.653(7) Å]. This is HO*i*Pr (O22) in the case of Ln2Ti6 (Scheme 1, right). The long Ti3–O22 distance of 2.158(4) Å indicates that the hydrogen atom is closer to the O*i*Pr group.

Each of the other OMc ligands in Ln2Ti6 bridges two metal atoms. The lanthanide ion and each Ti atom of the same asymmetric unit are bridged by one OMc ligand and by two OMc ligands to Ti1′ of the other asymmetric unit [La1–O4, La1–O10 2.545(4), La1–O12 2.458(4), Ti1–O5

2.004(3), Ti2–O11 1.954(3), Ti3–O13 1.944(4), Ti1′–O7 1.977(3), Ti1′–O9 1.990(3) Å]. The remaining OMc ligands connect the [TiO₆] octahedra to each other.

The reaction of Ln(OAc)₃ (Ln = La, Ce), Ti(O*i*Pr)₄ and methacrylic acid with a higher proportion of Ti(O*i*Pr)₄ than that used for the preparation of La2Ti6 or Ce2Ti6 resulted in the formation of LnTi₄O₃(O*i*Pr)₂(OMc)₁₁ (LaTi4 and CeTi4, Figure 3). The clusters are isomorphous and isostructural, and therefore the bond lengths and angles will only be discussed for LaTi4. Crystals of LnTi4 contain two independent clusters in the asymmetric unit (atom labels La1/Ti1–Ti4 and La2/Ti5–Ti8, respectively). One of them shows disorder of the central Ln atom and one Ti atom (70:30 occupancy). La2A is shifted by 0.262(5) Å from the original La2 position towards Ti8, which is also disordered [Ti8–Ti8A 0.412(8) Å]. This also affects the OMc ligands bridging La2/Ti8 and Ti5/Ti6, as well as the terminal O*i*Pr group on Ti8 and the second O*i*Pr group on Ti5. Apart from this disorder the two clusters are equivalent in composition and coordination.
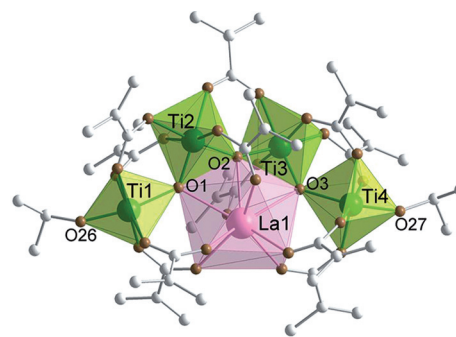

Figure 3. Molecular structure of LaTi₄(μ₃-O)₃(O*i*Pr)₂(μ₂-OMc)₁₁ (LaTi4) Hydrogen atoms are omitted or clarity. Selected bond lengths [Å] and angles [°]: La1–O1 2.6410(18), La1–O2 2.4793(17), La1–O3 2.6228(18), La1–O4 2.5455(18), La1–O6 2.447(2), La1–O8 2.5447(19), La1–O10 2.558(2), La1–O12 2.533(2), 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), Ti1–O26 1.782(2), Ti2–O1 1.7904(18), Ti2–O2 1.8249(18), Ti2–O9 1.981(2), Ti2–O17 2.056(2), Ti2–O19 2.019(2), Ti2–O20 2.0826(19), Ti3–O2 1.8409(18), Ti3–O3 1.7786(18), Ti3–O11 1.975(2), Ti3–O21 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)°, La1–O1–Ti1 126.53(8), La1–O1–Ti2 100.45(7), Ti1–O1–Ti2 132.00(10), La1–O2–Ti2 105.50(7), La1–O2–Ti3 105.34(8), Ti2–O2–Ti3 149.13(10), La1–O3–Ti3 101.80(8), La1–O3–Ti4 123.24(8), Ti3–O3–Ti4 132.39(10).

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 [TiO₆] 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 4.1282(6), La1–Ti4 4.0530(6), La1–Ti2 3.4489(5), La1–Ti3 3.4571(7) Å]. Each of the three μ₃-O atoms link two [TiO₆] 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

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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 O*i*Pr 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 $Sr_2Ti_8O_8(OiPr)_2(OAc)_2(OMc)_{16}$ and $Pb_2Ti_8O_8(OBu)_2(OMc)_{18}(BuOH)_2$, 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 $[TiO_6]$ octahedron is condensed to the Ln atom instead of there being a "dimerization" of the LnTi3 unit by condensation of two $[LnO_8]$ 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 $Ln_2Ti_4O_4(OMc)_{14}(HOMc)_2$ (Ln2Ti4) were formed with the smaller ions (ion radii 1.02–1.08 Å), and clusters with the composition $Ln_2Ti_6O_6(OiPr)_2(OMc)_{16}(HOMc)_2$ (Ln2Ti6) were formed with the larger ions (ion radii 1.08–1.16 Å for coordination number 8). Sm with a radius of 1.08 Å is a borderline case as both clusters can be formed. The increasing ion radii are also reflected in the increasing M–O bond lengths. The comparison shows that small variations in the ion radii of the second metal may result in different structures of the M/Ti mixed-metal clusters.

The larger ions allow coordination of an additional $[TiO_6]$ unit (with concomitant partial rearrangement of the ligand sphere). An increase in the ion radii is of course closely associated with the ability to increase the coordination number of the metal. Although the Ln atom in Ln2Ti4 is clearly eight-coordinate, that in Ln2Ti6 is between eight- and nine-coordinate (eight stronger Ln–O bonds and one weak interaction). This is also seen for the alternatively formed clusters $LaTi_4O_3(OiPr)_2(OMc)_{11}$ with the largest Ln^{3+} ions (LaTi4 and Ce2Ti4) in which the coordination

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
La^{3+}	9	1.216	2.45–2.64	LaTi4O3
Ce^{3+}	9	1.196	2.42–2.62	CeTi4O3
La^{3+}	8	1.16	2.46–2.55	La2Ti6O6
Ce^{3+}	8	1.143	2.41–2.53	Ce2Ti6O6
Nd^{3+}	8	1.109	2.38–2.51	Nd2Ti6O6
Sm3+	8	1.079	2.31–2.57	Sm2Ti6O6
			2.32–2.51	Sm2Ti4O4
Eu^{3+}	8	1.066	2.32–2.49	Eu2Ti4O4
Gd^{3+}	8	1.053	2.27–2.51	Gd2Ti4O4
Ho^{3+}	8	1.015	2.28–2.52	Ho2Ti4O4
Y^{3+}	8	1.019	2.28–2.55	Y2Ti4O4

number of the Ln atom is nine. An interesting side aspect of this work is that no acetate and only methacrylate ligands are incorporated into the clusters.

Experimental Section

General: All experiments were carried out under Ar by using standard Schlenk techniques. $Y(OAc)_3 \cdot xH_2O$, $La(OAc)_3 \cdot xH_2O$, $Ce(OAc)_3 \cdot xH_2O$, $Eu(OAc)_3 \cdot xH_2O$, $Sm(OAc)_3 \cdot xH_2O$ and $Gd(OAc)_3 \cdot xH_2O$, were obtained from Aldrich. $Ti(OiPr)_4$, $Ho(OAc)_3 \cdot H_2O$ and $Nd(OAc)_3 \cdot xH_2O$ 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 ^{13}C NMR spectra in solution were recorded with a Bruker Avance 250 spectrometer [250.13 MHz (^1H), 62.86 MHz (^{13}C)] 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^{-4} on a diamond ATR unit.

X-ray Crystallography: Crystallographic data were collected with a Bruker AXS SMART APEX II four-circle diffractometer with κ geometry at 100 K by using Mo-K_α (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 symmetries were 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 F^2 (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. Crystal data, data collection parameters and refinement details are listed in Tables 2, 3 and 4. Although all structures of the Ln2Ti4 clusters could be refined to satisfying values despite the disorder described before, there was still some unresolved electron density. The highest residual electron density was observed close to a methacrylic acid. The distances of this peak to any of the atoms or other unresolved electron density maxima do not fit with any chemical entity. When the data were cut at lower degrees, the electron density of this maximum decreased. It was nevertheless observed in all X-ray experiments on the Ln2Ti4 clusters, although different crystals were investigated. Such a resid-

ual electron density was not mentioned in the literature for the isostructural Y2Ti4.[5] Therefore, the cluster was prepared again with Y(OAc)$_3$ as precursor. The structure was re-determined, and no such electron density was observed. Hence the unresolved electron density in the Ln2Ti4 clusters is most probably a feature related to the Ln ions and not caused by some disorder or partial substitution of ligands. Two clusters of equal composition and structure crystallized in the unit cell of LnTi4. One of these clusters showed positional disorder. The crystal was therefore checked for twinning. The crystal was clearly triclinic, therefore only non-merohedral twinning was possible. Examination of the diffraction pattern showed only separated and well-defined reflections. As was observed for both LaTi4 and CeTi4, this appears to be a feature of this structure. CCDC-1014141 (for Sm2Ti4), -1014142 (for Eu2Ti4), -1014143 (for Gd2Ti4), -1014144 (for Ho2Ti4), -1014145 (for La2Ti6), -1014146 (for Ce2Ti6), -1014147 (for Nd2Ti6), -1014148 (for Sm2Ti6), -1014149 (for LaTi4) and -1014150 (for CeTi4) 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.

General Synthetic Procedure: Ti(OiPr)$_4$, 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$_2$Ti$_4$O$_4$(OMc)$_{14}$(HOMc)$_2$ (Y2Ti4): Y(OAc)$_3$ (1 mmol, 0.266 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. Orange crystals were isolated after 1 week. Yield: 0.51 g (57 % based on Y). IR: ṽ = 2979 (w), 2961 (w), 2928 (w), 1697 (w), 1643 (w), 1563 (s), 1454 (m), 1385 (s), 1368 (s), 1232 (s), 1007 (m), 938 (m), 852 (w), 826 (s), 760 (s), 654 (m) cm^{-1}.

Sm$_2$Ti$_4$O$_4$(OMc)$_{14}$(McOH)$_2$ (Sm2Ti4): Sm(OAc)$_3$ (2 mmol, 0.955 g) was mixed with Ti(OiPr)$_4$ (2 mmol, 0.568 g) and methacrylic acid (18 mmol, 1.55 g). The solution was stirred for 1 d. Pale-yellow crystals were isolated after 2 weeks. Yield: 0.352 g (37 %

based on Sm). The same cluster was obtained when Sm/Ti/McOH molar ratios of 2:1:13.5 and 1:2:13.5 were employed. ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ = 1.52–1.80 (m, 6 H, CH$_3$), 1.97 (br. s, 30 H, CH$_3$), 2.19–2.70 (m, 12 H, CH$_3$), 5.22–5.58 (m, 5 H, CH$_2$), 5.70 (br., s, 10 H, CH$_2$), 5.88–6.05 (m, 3 H, CH$_2$), 6.25 (br. s, 10 H, CH$_2$), 6.48–7.09 (m, 4 H, CH$_2$), 8.67 (br. s, 2 H, COOH) ppm. IR: ṽ = 2978 (w), 2927 (w), 1698 (w), 1643 (w), 1562 (s), 1454 (m), 1364 (s), 1231 (s), 1122 (w), 1007 (m), 937 (m), 851 (m), 825 (m), 739 (s), 656 (w), 615 (m) cm^{-1}.

Eu$_2$Ti$_4$O$_4$(OMc)$_{14}$(HOMc)$_2$ (Eu2Ti4): Eu(OAc)$_3$ (1 mmol, 0.329 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. 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(OiPr)$_4$ (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: ṽ = 2979 (w), 2927 (w), 1697 (w), 1643 (w), 1560 (s), 1454 (m), 1384 (s), 1367 (s), 1232 (s), 1006 (m), 937 (m), 851 (w), 826 (s), 754 (s), 653 (w), 601 (s) cm^{-1}.

Gd$_2$Ti$_4$O$_4$(OMc)$_{14}$(HOMc)$_2$ (Gd2Ti4): Gd(OAc)$_3$ (1 mmol, 0.334 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. Pale-orange crystals were isolated after 1 week. Yield: 0.686g (71 % based on Gd). This cluster was also obtained with Gd/Ti ratios of 1:1 and 2:1 in the precursor mixture. IR: ṽ = 2979 (w), 2927 (w), 1698 (w), 1664 (w), 1644 (w), 1561 (s), 1454 (m), 1384 (s), 1367 (s), 1232 (s), 1129 (w), 1006 (m), 937 (m), 852 (w), 825 (s), 758 (s), 653 (m), 601 (s) cm^{-1}.

Ho$_2$Ti$_4$O$_4$(OMc)$_{14}$(HOMc)$_2$ (Ho2Ti4): Ho(OAc)$_3$ (1 mmol, 0.342 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. Orange crystals were isolated after 1 week. Yield: 0.756g (78 % based on Ho). This cluster was also obtained with Ho/Ti ratios of 1:1 and 2:1 in the precursor mixture. IR: ṽ = 2979 (w), 2961 (w), 2929 (w), 1697 (w), 1643 (w), 1561 (s), 1530 (s), 1455 (m), 1388 (s),

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

	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	t6riclinic
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)	12.3566(14)
c [Å]	14.521(3)	14.5215(10)	14.436(4)	14.470(2)
α [°]	84.326(5)	84.291(2)	84.773(5)	84.292(3)
β [°]	82.168(5)	82.203(2)	81.557(6)	82.373(3)
γ [°]	77.779(5)	77.637(2)	77.591(5)	77.239(2)
V [Å^3]	1979.3(6)	1977.5(2)	1967.4(10)	1962.1(4)
Z	1	1	1	1
D_x [Mg m^{-3}]	1.609	1.615	1.632	1.649
μ [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	0.22 × 0.19 × 0.18
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. [$I > 2\sigma(I)$]	71616, 9215, 7690	87054, 12723, 9772	91177, 11236, 10189	86970, 11125, 9310
R_{int}	0.0435	0.0495	0.0634	0.0583
θ_{max} [°]	27.71	31.18	29.82	29.74
$R[F^2 > 2\sigma(F)]$, $\omega R(F^2)$, S	0.041, 0.087, 1.147	0.036, 0.096, 1.100	0.422, 0.107, 1.119	0.035, 0.098, 1.186
Weighting scheme[a]	$x = 0.0178$, $y = 11.8006$	$x = 0.0334$, $y = 2.9260$	$x = 0.0528$, $y = 6.0150$	$x = 0.0277$, $y = 6.4784$
$\delta\rho_{max}$, $\delta\rho_{min}$ [e Å^{-3}]	3.549, –1.416	2.573, –1.077	1.904, –1.705	3.804, –1.640

[a] $\omega = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, in which $P = (F_o^2 + 2F_c^2)/3$.

Table 3. Crystal data, data collection parameters and refinement details of Ln2Ti6.

	La2Ti6	Ce2Ti6	Nd2Ti6	Sm2Ti6
Empirical formula	$C_{78}H_{106}La_2O_{44}Ti_6$	$C_{78}H_{106}Ce_2O_{44}Ti_6$	$C_{78}H_{106}Nd_2O_{44}Ti_6$	$C_{78}H_{106}Sm_2O_{44}Ti_6$
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(13)	16.1410(5)	16.1458(10)	16.2144(8)
β [°]	113.483(4)	113.5940(10)	113.847(2)	113.897(2)
V [Å³]	4975.0(7)	4974.8(3)	4961.9(5)	4984.1(4)
Z	2	2	2	2
D_x [Mg m⁻³]	1.544	1.546	1.550	1.556
μ [mm⁻¹]	1.381	1.437	1.570	1.700
Crystal size [mm]	$0.30 \times 0.27 \times 0.22$	$0.35 \times 0.22 \times 0.20$	$0.38 \times 0.28 \times 0.23$	$0.45 \times 0.38 \times 0.30$
T_{min}, T_{max}	0.6821, 0.7509	0.6331, 0.7620	0.5869, 0.7141	0.5151, 0.6296
No. measd., indep., obsd. refl. [$I > 2\sigma(I)$]	235033, 15865, 12066	253922, 17295, 13604	315033, 20740, 14016	318094, 20940, 17821
R_{int}	0.035	0.064	0.0479	0.0429
θ_{max} [°]	31.14	32.32	34.48	34.75
$R[F^2 > 2\sigma(F)]$, $\omega R(F^2)$, S	0.062, 0.140, 1.353	0.045, 0.114, 1.213	0.068, 0.168, 1.255	0.045, 0.100, 1.317
Weighting scheme[a]	$x = 0.0134$, $y = 19.2502$	$x = 0.0331$, $y = 8.4502$	$x = 0.0337$, $y = 19.5161$	$x = 0.0184$, $y = 11.8747$
$\delta\rho_{max}$, $\delta\rho_{min}$ [e Å⁻³]	1.752, –1.350	1.374, –1.352	2.207, –1.815	2.255, –1.540

[a] $\omega = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, in which $P = (F_o^2 + 2F_c^2)/3$.

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

	LaTi4	CeTi4
Empirical formula	$C_{50}H_{69}LaO_{27}Ti_4$	$C_{50}H_{69}CeO_{27}Ti_4$
M_r	1432.56	1433.66
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	11.8330(6)	11.7983(10)
b [Å]	12.8405(7)	12.9135(12)
c [Å]	41.567(2)	41.763(4)
α [°]	84.8600(10)	84.820(2)
β [°]	85.8980(10)	86.530(2)
γ [°]	89.2520(10)	89.790(2)
V [Å³]	6274.0(6)	6325.2(10)
Z	4	4
D_x [Mg m⁻³]	1.517	1.506
μ [mm⁻¹]	1.233	1.267
Crystal size [mm]	$0.36 \times 0.34 \times 0.30$	$0.35 \times 0.28 \times 0.21$
T_{min}, T_{max}	0.6841, 0.7464	0.6773, 0.7459
No. measd., indep., obsd. refl. [$I > 2\sigma(I)$]	217332, 36907, 30664	210874, 34198, 28928
R_{int}	0.034	0.051
θ_{max} [°]	30.15	29.68
$R[F^2 > 2\sigma(F)]$, $\omega R(F^2)$, S	0.048, 0.011, 1.159	0.039, 0.087, 1.10
Weighting scheme[a]	$x = 0.0308$, $y = 10.2792$	$x = 0.0258$, $y = 7.7332$
$\delta\rho_{max}$, $\delta\rho_{min}$ [e Å⁻³]	0.972, –1.086	1.164, –0.916

[a] $\omega = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, in which $P = (F_o^2 + 2F_c^2)/3$.

1371 (s), 1231 (s), 1006 (m), 942 (m), 868 (m), 851 (w), 829 (s), 761 (m), 658 (m), 601 (s) cm⁻¹.

La₂Ti₆O₆(OMc)₁₈(HOiPr)₂ (La2Ti6): La(OAc)₃ (2 mmol, 0.632 g) was mixed with Ti(OiPr)₄ (2 mmol, 0.568 g) and methacrylic acid (18 mmol, 1.550 g). The solution was stirred for 1 d. Orange crystals were isolated after 2 weeks. The same cluster was obtained with an La/Ti ratio of 2:1 in the precursor mixture. Yield: 0.324 g (84% based on Ti). ¹H NMR (CD₂Cl₂, 250 MHz): δ = 1.17–1.28 (m, 12 H, CH₃, HOiPr), 1.62–2.09 (m, 54 H, CH₃, OMc), 4.02 (sept., 2 H, CH, HOiPr), 5.29–5.67 (m, 18 H, =CH₂, OMc), 5.89–6.23 (m, 18 H, =CH₂, OMc) ppm. ¹³C NMR (CD₂Cl₂, 250 MHz): δ = 17.6–18.0 (CH₃, OMc), 25.0 (CH₃, HOiPr), 64.3–64.6 (CH, HOiPr), 127.4 (CH₂, OMc), 138.4 (C, OMc), 172.8 (COO, OMc) ppm. IR: $\tilde{\nu}$ = 3098 (w), 2976 (w), 2957 (w), 2927 (w), 1697 (w), 1643 (w),

1563 (s), 1543 (s), 1503 (w), 1453 (m), 1385 (s), 1363 (vs), 1327 (m), 1232 (s), 1121 (w), 1045 (w), 1007 (m), 940 (m), 849 (w), 827 (m), 807 (m), 745 (s), 656 (m), 612 (s) cm⁻¹.

Ce₂Ti₆O₆(OMc)₁₈(HOiPr)₂ (Ce2Ti6): Ce(OAc)₃ (1 mmol, 0.317 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. Orange crystals were isolated after 2 weeks. The same cluster was also obtained with Ce/Ti ratios of 1:1 and 2:1 in the precursor mixture. Yield: 0.305 g (79% based on Ti). ¹H NMR (CD₂Cl₂, 250 MHz): δ = 1.17–1.28 (m, 12 H, CH₃, HOiPr), 1.62–2.08 (m, 54 H, CH₃, OMc), 4.01 (sept, 2 H, CH, HOiPr), 5.33–5.68 (m, 18 H, =CH₂, OMc), 6.05–6.22 (m, 18 H, =CH₂, OMc) ppm. ¹³C NMR (CD₂Cl₂, 250 MHz): δ = 17.6 (CH₃, OMc), 25.0 (CH₃, HOiPr), 64.4–67.8 (CH, HOiPr), 124.4–127.3 (CH₂, OMc), 136.0–138.9 (C, OMc),

172.5 (COO, OMc) ppm. IR: ṽ = 2975 (w), 2927 (w), 1698 (w), 1645 (m), 1601 (m), 1577 (s), 1516 (m), 1454 (m), 1414 (s), 1385 (s), 1365 (s), 1235 (m), 1162 (w), 1123 (m), 1104 (m), 936 (m), 857 (s), 825 (m), 741 (m), 659 (m) cm^{-1}.

Nd$_2$Ti$_6$O$_6$(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: ṽ = 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}.

Sm$_2$Ti$_6$O$_6$(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). ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ = 1.19–1.34 (m, 12 H, CH$_3$, HOiPr), 1.69 (s, 3 H, CH$_3$, OMc), 1.76–2.36 (m, 51 H, CH$_3$, OMc), 4.60–4.80 (m, 2 H, CH, HOiPr), 5.34–5.92 (m, 18 H, =CH$_2$, OMc), 6.31–6.80 (m, 18 H, =CH$_2$, OMc) ppm. IR: ṽ = 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), 1006 (m), 932 (m), 852 (w), 832 (m), 692 (m), 659 (w) cm^{-1}.

LaTi$_4$O$_3$(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: 0.567g (79 % based on La). ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ = 1.19–1.28 (m, 12 H, CH$_3$, OiPr), 1.62–2.08 (m, 33 H, CH$_3$, OMc), 4.02 (sept, 2 H, CH, OiPr), 5.29–5.68 (m, 11 H, =CH$_2$, OMc), 5.90–6.13 (m, 11 H, =CH$_2$, OMc) ppm. IR: ṽ = 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}.

CeTi$_4$O$_3$(OiPr)$_2$(OMc)$_{11}$ (CeTi4): Ce(OAc)$_3$ (1 mmol, 0.317 g) was mixed with Ti(OiPr)$_4$ (6 mmol, 1.705 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).

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