Two new hexanuclear titanium oxo cluster types and their structural connection to known clusters

Matthias Czakler, Christine Artner and Ulrich Schubert

The robustness of the Ti₆O₆(OPr)₆(OOCR)₀ structure type is also demonstrated by the fact that the structures of many mixed-metal clusters are derived from this lead structure. The four cluster types with a Ti₆O₆ core vary by different d₄ and d₅. Ti₆O₆(OPr)₆(OOCR)₀ is the second most common Ti₆ cluster type, with a higher d₄ and a lower d₅ than Ti₆O₆(OPr)₆(OOCR)₀. The two types of Ti₆O₆(OPr)₂(OOCR)₄ clusters are only represented by a few examples. The different proportion of terminal, μ₂ and μ₃ ligands (μ₂-O in Ti₆O₆(OEt)₁₄(OOCPh)₁₂ is a very rare exception) in the Ti₆O₆ clusters results in different structures, i.e. in a different linkage of the [TiO₆] octahedra. There is only one example for a cluster with a Ti₆O₅ core, Ti₆O₅(OiBu)₁₄(OOCBu)₁₆ which is structurally derived from the Ti₆O₆(OPr)₆(OOCR)₀ structure by the (formal) replacement of two terminal OR groups by a μ₂-O.

Introduction

Reaction of Ti(OR)₄ with carboxylic acids results in the formation of carboxylate-substituted oxo clusters with a broad range of nuclearities. In such reactions, partial or complete substitution of the OR groups by carboxylate ligands and generation of oxo groups through ester formation between the carboxylic acid and the eliminated alcohol compete with each other. The degree of substitution (d₄ = RCOO/Ti ratio) and the degree of condensation (d₅ = O/Ti ratio) of the obtained clusters reflect the proportion of both reactions; they are key parameters for which structures are formed. In the case of titanium, μ₂-O count for full for the calculation of d₅, μ₃-O for 2/3 and μ₄-O for 4/3, because in rutile and anatase (d₅ = 2) every oxygen is μ₄-O.

Common to all Ti oxo clusters is that the Ti atoms are six-coordinate (rarely five-coordinate, see below) and the carboxylate ligands almost always bridge two Ti atoms. Stable clusters are obtained if the metal charges are balanced by the ligands and all available coordination sites are occupied. A large percentage of the (uncharged) carboxylate-substituted titanium oxo clusters are hexanuclear where the six octahedrally coordinated Ti atoms sum up to 24 positive charges and 36 coordination sites in total. The cluster cores of the known Ti₆ clusters are schematically shown in Scheme 1. The Ti₆ cluster type with the highest d₄ (and a wide variety of R/R’ combinations) is Ti₆O₆(OPr)₆(OOCR)₀ where all oxygen atoms are μ₄-O. This leaves 12 positive charges uncompensated and 18 coordination sites unoccupied which are compensated by 6 terminal OR (one per Ti) and 6 bridging carboxylate ligands.

The occurrence of Ti₆(μ₂-O) units in nearly all Ti oxo clusters, also in clusters with low d₄, is a strong indication that this unit is formed in an early stage of the condensation process.

In this article, we report two new structure types of Ti₆ oxo clusters (Scheme 2), which demonstrate the structural variability of this cluster class, depending on d₄ and d₅, but nevertheless have some features in common and thus complement the series of clusters shown in Scheme 1. Both contain Ti₃(μ₃-O) units as building blocks. As we have pointed out earlier (in an article on Ti₆O(OPr)₆(OOCR)₂ clusters) that the Ti₆O unit can be flat or pyramidal, without obvious correlation to other structural parameters. This possibly indicates that flat/pyramidal conversion is easy. To facilitate the comparison between the different cluster
structures we have drawn the Ti₃O units in Scheme 2, and all other Schemes in this article, in pyramidal conformations.

Results

Reaction of Ti(OiPr)₄ with 4 molar equivalents of cyclobutane carboxylic acid resulted in the formation of Ti₆O₆(OiPr)₂(OOCC₄H₇)₁₀ (1a, Fig. 1). An isostructural cluster, Ti₆O₆(OiPr)₂(OOCEt)₁₀ (1b) was obtained as a minor side-product in a different reaction, which shows that 1a is not an isolated case.

There are no significant structural differences between 1a and 1b. The centrosymmetric structures consist of six roughly coplanar titanium atoms. Two Ti₃O units, with nearly trigonal-planar μ₃-O atoms (sum of angles 354.6°), are bridged by two μ₂-O and four carboxylate ligands. The Ti/O core structure is basically the same as that of the Ti₆O₆(OR)₂(OOCR')₆ clusters (Scheme 1), but the two bridging OR groups in the Ti₆O₆ clusters are replaced by μ₂-O atoms. This replacement, however, also affects the bystander ligands, because the Ti charges must be balanced and all coordination sites occupied. To keep the cluster uncharged, two additional singly charged ligands (OR) must be removed, which, however, leaves two coordination sites unoccupied. Therefore two further terminal (OR) groups must be replaced by two bridging (carboxylate) ligands.

For this reason, the arrangement of ligands decorating the Ti₆O₆ cluster core in 1 is slightly different compared to Ti₆O₆(OR)₂(OOCR')₆. Only the outer Ti atoms (Ti1 and symmetry-related Ti1* in 1a) of the ellipse-shaped Ti₆ arrangement still carry...
a terminal OiPr group (these atoms are substituted by two terminal OR ligands in the Ti₆O₄ clusters). All the other coordination sites are occupied by oxygen atoms of bridging carboxylate ligands. Thus, Ti₁ and Ti₂ are coordinated by three bridging carboxylate ligands, and Ti₃ by four. This results in the highest dₙ among all the Ti₆ oxo clusters. In passing, the highest possible dₙ for Ti oxo clusters (with 6-coordinate Ti atoms) is 2 as in [TiO(OOCR)₆]²⁺.34

The Ti₁O group in 1 is quite unsymmetrical, the Ti₁–O₁ distance being much longer than Ti₂–O₁ and Ti₃–O₁ and, correspondingly, Ti₂–O₁–Ti₃* being much larger than Ti₂–O₁–Ti₁ and Ti₃–O₁–Ti₁. This distortion of the Ti₆O₄ cluster is also observed in the Ti₆O₄(OEt)₈(OOCR)₈ clusters and possibly due to the terminal OR group being trans to Ti₁–O₁ (for example in Ti₆O₄(OEt)₈(OOCR)₈ clusters). One terminal OR ligand is missing and the two Ti₁O entities. This oxygen (O₃ and O₃*) in 1a is trans to another bridging oxygen (O₂, which is essentially symmetrically located between Ti₁ and Ti₂) at Ti₂ in 1a, but trans to a bridging OR group in Ti₆O₄(OEt)₈(OOCR)₈. While O₃ in 1a is shifted away from Ti₂ (Ti₂–O₃ 2.003(3), Ti₃–O₃ 1.722(3) Å), the oxygen bridging the two Ti entities in Ti₆O₄(OEt)₈(OOCR)₈ is shifted towards the respective Ti atom (with a smaller difference between both Ti–O distances). This is apparently due to a different trans influence of µ₂-O compared with µ₂-OR. The pronounced asymmetry of the Ti₂–O₃–Ti₃ arrangement in 1a also affects bonding of the carboxylate ligand bridging Ti₁ and Ti₃*, with Ti₁–O₁ (2.010(4) Å) is shorter and Ti₃–O₈ (2.152(3) Å) much longer than the other carboxylate Ti–O distances (2.010(4)–2.063(3) Å).

The situation in solution is hard to comprehend, because the number of signals of 1a in both the ¹H and ¹³C solution NMR spectra at ambient temperature corresponds neither to the solid-state structure nor to a fully dynamic situation. Most striking is that two sets of signals of equal intensity are observed in the ¹H NMR spectrum if the structure is static in solution. Although only four groups can be clearly resolved and the other ten groups only give a broad range of signals in the CH₃ region of

moisture in the system. We nevertheless report the structure of 2 here, because it nicely complements the structural series of known Ti₆ clusters.

Type II Ti₆O₄(OR)₁₂(OOCR)₁₄ clusters consist of two Ti₆O₄/OR₆(OOCR)₆ units (with Ti₆O₄/OR₆ cores) which are connected by two µ₂-O. The building blocks of cluster 2 are the same Ti₆O₄ clusters, but connected by one µ₂-O and two bridging dicarboxylate ligands. The structure of 2 (Fig. 2) can thus formally be derived from the Ti₆O₄ cluster type by removing one µ₂-O between the Ti₆O₄ units and replacing the second µ₂-O by a µ₂-O (compare Schemes 1 and 2). Charges and coordination sites are compensated by additional carboxylate groups. The substitution pattern of the bystander ligands in the Ti₆O₄ units of 2 is essentially the same as in Ti₆O₄(OiPr)₈(OOCPh)₆ and Ti₆O₄(OCH₂CMe₂)₈(OOCH)₂.5 Another way of looking at the structure of 2 therefore is that two such Ti₆O₄ clusters are bridged by a µ₂-O (O₃), where the µ₂-O replaces a terminal OR ligand in each Ti₆O₄ cluster unit (see Discussion section).

One Ti atom in each Ti₆O₄ unit (Ti₃ and Ti₆) is 5-coordinate, as in the reference Ti₆O₄ structures. Interestingly, the 5-coordinate Ti atoms are in geometrically different positions: in one unit (Ti₁~Ti₃) this is Ti₃, bonded to the bridging oxygen O₃, and in the second (Ti₄~Ti₆) Ti₆ which is only bridged to one of its neighbors by a µ₂-OR group. Correspondingly, the bridging O₃ atom is closer to the 5-coordinate Ti atom (Ti₃–O₃ 1.780(2) Å) than to Ti₄ (Ti₄–O₃ 1.849(2) Å), and the Ti–O distances between the two oxygens O₁ and O₂ and the 5-coordinate Ti atoms (Ti₃–O₁ 1.860(2), Ti₆–O₂ 1.844(3) Å) are shorter than to the 6-coordinate ones (1.797(2)–2.005(3) Å). Because 2 has no molecular symmetry, fourteen different groups of signals of the OiPr groups are expected in the ¹H NMR spectrum if the structure is static in solution. Although only four groups can be clearly resolved and the other ten groups only give a broad range of signals in the CH₃ region of

We have shown previously that reaction of Ti(OiPr)₄ with an equimolar amount of phthalic anhydride resulted in transfer of an OiPr group from the metal to one carbonyl group of the anhydride and coordination of the thus formed phthalic monoester to titanium to give Ti₃(OiPr)₆(OOC–CMe–CH–COO)₂(OiPrOH).15

In the analogous reaction of Ti(OiPr)₄ with maleic anhydride we now isolated a small proportion of Ti₆O₄(OiPr)₈(OOCR)₈ clusters (denoted as Ti₆O₄(OiPr)₈(OOCR)₈ in Scheme 1 for comparison with monocarboxylate ligands). This compound was almost certainly formed by the unintentional introduction of

![Fig. 2 Molecular structure of Ti₆O₄(OiPr)₈(OOCC–CH=CH–COO)₂ (2)](image)

Selected bond distances [Å] and angles [°]: Ti₁–O₁ 1.997(2), Ti₂–O₁ 1.981(2), Ti₃–O₁ 1.860(2), Ti₄–O₂ 1.981(2), Ti₅–O₂ 2.005(3), Ti₆–O₂ 1.844(3), Ti₃–O₃ 1.780(2), Ti₄–O₃ 1.849(2), Ti₅–O₁–Ti₁ 144.5(1), Ti₁–O₁–Ti₂ 105.3(1), Ti₄–O₂–Ti₆ 144.1(1), Ti₅–O₂–Ti₆ 107.0(1), Ti₄–O₂–Ti₅ 154.3(1), Ti₃–O₃–Ti₄ 156.6(1).
the spectrum this appears to be the case. The CH is also not resolved. An assignment of the signals to specific OiPr groups is therefore not possible.

Discussion

Various types of carboxylate-substituted titanium oxo clusters have been isolated from reactions of titanium alkoxides with carboxylic acids. Clusters of a particular composition and structure are reproducibly formed, if the precursors and reaction conditions stay meticulously the same. While the structure of a given cluster can be rationalized, as discussed in the Introduction, it is currently not possible to predict which cluster type will be formed in a particular reaction environment. This is due to the fact that substitution and condensation reactions compete with each other and the relative rates of both reactions are influenced by a number of parameters, among them the electronic and steric properties of the groups R and R’ and the Ti(OR)/R’COOH ratio. Furthermore, the reactions cannot be monitored in situ, because the IR and NMR spectra are largely uninformative. The isolation of a specific cluster from a reaction mixture (possibly containing different cluster species) could therefore also be due to a higher crystallization tendency.

However, comparative analysis of different cluster structures may give clues on how the structures develop during the reactions. We have discussed in a previous article that stable Ti₆O₄(OR)₈(OOCR)₂ clusters are apparently only obtained if the groups R or R’ are bulky. The occurrence of Ti₆O₄ units in the majority of Ti oxo clusters with dₑ ≤ 1 indicates that Ti₆O₄ clusters are formed early in the reactions and serve – if not stabilized by bulky groups – as building blocks for the thermodynamically favored products Ti₆O₄(OR)₈(OOCR)₁₆ ([−TiO(OR)(OOCR)]₈) and Ti₆O₄(OOCR)₂ (type II) can similarly be interrelated (Scheme 3). Ti₆O₄(OR)₈(OOCR)₄ is structurally derived from a formal condensation of two Ti₆O₄ clusters. The structure of Ti₆O₄(OR)₄(OOCR)₄ can similarly be converted into that of Ti₆O₄(OR)₂(OOCR)₄ by intramolecular condensation of two OR groups with concomitant conversion of μ₂-O into μ₂-O, by which all Ti atoms become 6-coordinate. Note again that this only a structural discussion, and formation of the clusters may proceed differently, especially in the case of 2, where a dicarboxylate group is involved, rather than two monocarboxylate ligands.

Experimental

General

All experiments were carried out under Ar atmosphere using standard Schlenk techniques. Ti(OiPr)₄ was obtained from ABCR. All solvents used for NMR spectroscopy (Eurisotop) were degassed prior to use and stored over molecular sieve. ¹H and ¹³C solution NMR spectra were recorded on a Bruker AVANCE 250 (250.13 MHz [¹H], 62.86 MHz [¹³C]) equipped with a 5 mm inverse-broadband probe head and a z-gradient unit.

Synthesis of Ti₈O₆(OiPr)₄(OOCCH₃)₂

Ti(OiPr)₄ (0.31 ml, 1 mmol) was slowly added to 0.38 ml (4 mmol) of cyclobutane carboxylic acid under stirring. A clear solution was obtained of which crystals of 1a were obtained after 3 weeks. Yield 80 mg (32%). ¹H NMR (CDCl₃, 250 MHz) δ (ppm) 1.22 (d, J = 6.28 Hz, 6H, CHCH₃), 1.31 (d, J = 6.12 Hz, 6H, CHCH₃), 1.73-2.05 (m, 20H, CH₂CH₂CH₂CH₂), 2.06-2.50 (m, 40H, CH₂CH₂), 2.95-3.11 (m, 5H, C₂H₅COCH₃), 3.14-3.33 (m, 5H, C₂H₅COCH₃), 3.14-3.33 (m, 5H, C₂H₅COCH₃).

Scheme 3 Interrelation of the cluster core structures of Ti₆O₄ and Ti₆O₆ with that of Ti₆O₄. The new groups/bonds are drawn in bold. The conformation of the cluster cores are drawn to emphasize structural similarities to the clusters in Schemes 1 and 2.
Scheme 4  Intercalation of the cluster core structures of Ti₆O₃, Ti₆O₃ and Ti₆O₄ (type II). The new bonds/groups are drawn in bold. The conformation of the cluster cores are drawn to emphasize structural similarities to the clusters in Schemes 1 and 2.

Table 1  Crystal data, data collection parameters and refinement details

|        | 1a                  | 1b                  | 2                  |
|--------|---------------------|---------------------|-------------------|
| Ω      | C₅₆H₈₂O₂₈Ti₆       | C₃₆H₆₄O₂₈Ti₆       | C₅₀H₁₀₂O₂₅Ti₆    |
| M (g/mol) | 1490.6             | 1232.3             | 1390.7            |
| Crystal system | Triclinic           | Triclinic           | Triclinic        |
| Space group | P₁                 | P₁                 | P₁               |
| a (Å) | 12.9095(7)          | 11.467(2)          | 15.6563(3)       |
| b (Å) | 12.9095(7)          | 11.467(2)          | 15.6563(3)       |
| c (Å) | 9.6136(4)           | 9.363(1)           | 12.9095(7)       |
| α (°) | 100                 | 100                 | 295              |
| β (°) | 96.711(2)           | 93.427(8)          | 83.25(4)         |
| γ (°) | 112.864, 5603, 3421 | 75.625(7)          | 76.797(1)        |
| V (Å³) | 1601.5(1)           | 1277.0(4)          | 3655.3(1)        |
| Dₓ (g cm⁻³) | 1.546               | 1.602              | 1.264            |
| μ (mm⁻¹) | 0.797               | 0.981              | 0.690            |
| No. of parameters | 436                 | 323                | 758              |
| Weighting scheme | x = 0.06587, y = 0.7700 | x = 0.0352, y = 0  | x = 0.0886, y = 2.9622 |
| Δρmax/Δρmin (e Å⁻³) | 0.912, -0.429       | 0.904, -0.914      | 0.969, -0.406    |

Synthesis of Ti₆O₃(OiPr)₁₄(OOC–CH=CH–COO)₂, 2

Ti(OiPr)₄ (8.8 ml, 30.3 mmol) was added to 2.96 g (30.1 mmol) of maleic anhydride in 9.3 ml of iPrOH. Crystals of 2 were obtained after 16 weeks at room temperature. Yield 200 mg (3%). ¹³C (¹H) NMR (CDCl₃, 62.9 MHz) δ (ppm) 18.24, 18.35, 18.52, 18.72 (CH₃CH₂), 21.79, 24.38 (CH₃CH₂), 25.14, 25.24, 25.29, 25.40, 25.46, 25.57, 25.61, 25.70 (CH₂CH₂), 37.38, 38.37, 39.47, 40.00, 40.14, 40.24 (CHCOO), 67.26, 77.19, 81.47 (CHMe₂), 180.80, 182.88, 184.38, 185.18, 185.78, 186.80 (COO).

X-ray structure analyses

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

The structures were solved by charge flipping (JANA2006). Refinement was performed by the full-matrix least-squares method based on F² (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 Table 1.

Conflicts of interest

There are no conflicts to declare.

References

1 Review: U. Schubert, J. Mater. Chem., 2005, 15, 3701–3715.
2 Review: L. Rozes and C. Sanchez, Chem. Soc. Rev., 2011, 40, 1006–1030.
3 P. Papiernik, L. G. Hubert-Pfalzgraf, J. Vaissermann and M. C. H. B. Goncalves, J. Chem. Soc., Dalton Trans., 1998, 2285–2287.
4 T. J. Boyle, T. M. Alam and C. J. Tafoya, Inorg. Chem., 1998, 37, 5588–5594.
5 T. J. Boyle, R. P. Tyner, T. M. Alam, B. L. Scott, J. W. Ziller and B. G. Potter, Jr., J. Am. Chem. Soc., 1999, 121, 12104–12112.
6 A. Pandey, V. D. Gupta and H. Noth, Eur. J. Inorg. Chem., 2000, 1351–1357.
7 A. Rammal, F. Brisach and M. Henry, C. R. Chim., 2002, 5, 59–66.
8 P. S. Ammala, S. R. Batton, C. M. Kepert, L. Spiccia, A. M. Van der Bergen and B. O. West, Inorg. Chim. Acta, 2003, 353, 75–81.
9 P. Piszczek, A. Grodzicki, M. Richert and A. Wojtczak, Inorg. Chim. Acta, 2004, 357, 2769–2775.
10 R. Sui, P. A. Charpentier, A. S. Rizkalla and M. C. Jennings, Acta Crystallogr., 2006, E62, m373–m375.
11 P. Piszczek, M. Richert and A. Wojtczak, Polyhedron, 2008, 27, 602–608.
12 P. Piszczek, M. Richert, A. Radtke, T. Muzioli and A. Wojtczak, Polyhedron, 2009, 28, 3872–3880.
13 J. B. Benedict and P. Coppens, J. Am. Chem. Soc., 2010, 132, 2938–2944.
14 G. A. Seisenbaeva, E. Ilina, S. Häkansson and V. G. Kessler, J. Sol–Gel Sci. Technol., 2010, 55, 1–8.
15 M. Czakler, C. Artner and U. Schubert, Eur. J. Inorg. Chem., 2012, 3485–3489.
16 P. Piszczek, A. Radtke, T. Muzioli, M. Richert and J. Chojnacki, Dalton Trans., 2012, 41, 8261–8269.
17 A. Radtke, P. Piszczek, T. Muzioli and A. Wojtczak, Inorg. Chem., 2014, 53, 10803–10810.
18 Y. Fan, Y. Cui, G.-D. Zou, R.-H. Duan, X. Zhang, Y.-X. Dong, H.-T. Lv, J.-T. Cao and Q.-S. Jing, Dalton Trans., 2017, 46, 8057–8064.
19 C. Artner, A. Koyun, M. Czakler and U. Schubert, Eur. J. Inorg. Chem., 2014, 5008–5014.
20 I. Gautier-Luneau, A. Mosset and J. Galy, Z. Kristallogr., 1987, 180, 83–95.
21 S. Doeuff, Y. Dromzee, F. Taulelle and C. Sanchez, Inorg. Chem., 1989, 28, 4439–4445.
22 I. Laaziz, A. Larbot, C. Guizard, J. Durand, L. Cot and J. Joffre, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 1990, 46, 2332–2334.
23 U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich and C. Chau, Chem. Mater., 1992, 4, 291–295.
24 B. Moraru, N. Hüsing, G. Kickelbick, U. Schubert, P. Fratzl and H. Peterlik, Chem. Mater., 2002, 14, 2732–2740.
25 G. Kickelbick, D. Holzinger, C. Brick, G. Trimmel and E. Moons, Chem. Mater., 2002, 14, 4382–4389.
26 Y. Gao, F. R. Kogler, H. Peterlik and U. Schubert, J. Mater. Chem., 2006, 16, 3268–3276.
27 P. Heinz, M. Puchberger, M. Bendova, S. O. Baumann and U. Schubert, Dalton Trans., 2010, 39, 7640–7644.
28 S. Doeuff, Y. Dromzee and C. Sanchez, C. R. Seances Acad. Sci., Ser. 2, 1989, 308, 1409–1412.
29 X. Lei, M. Shang and T. P. Fehlner, Organometallics, 1996, 15, 3779–3781.
30 X. Lei, M. Shang and T. P. Fehlner, Organometallics, 1997, 16, 5289–5301.
31 N. Steunou, F. Robert, K. Boubekeur, F. Ribot and C. Sanchez, Inorg. Chim. Acta, 1998, 279, 144–151.
32 I. Mijatovic, G. Kickelbick and U. Schubert, Eur. J. Inorg. Chem., 2001, 1933–1935.
33 M. Czakler and U. Schubert, Inorg. Chim. Acta, 2018, 471, 567–569.
34 C. Artner, M. Czakler and U. Schubert, Chem. – Eur. J., 2014, 493–498.
35 U. Schubert, Coord. Chem. Rev., 2017, 350, 61–67.
36 I. Mijatovic, G. Kickelbick, M. Puchberger and U. Schubert, New J. Chem., 2003, 27, 3–5.
37 U. Schubert, J. Mater. Chem., 2005, 15, 3701–3715, and references cited therein.
38 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Determination, University of Göttingen, Göttingen, Germany, 1997.