Methacrylate-Substituted Titanium-Yttrium Mixed-Metal Oxo Clusters

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Upon reaction of titanium propoxide and yttrium 2-methoxyethoxide with a sevenfold excess of methacrylic acid, three different mixed-metal clusters were obtained, depending on the titanium to yttrium alkoxide ratio. Clusters of the type $Ti_4Y_2(\mu_3\text{-}O)_4(\mu_2\text{-methacrylate})_{12}(\mu_1\text{-methacrylate})_2L_2$ (L = $MeOCH_2CH_2OH$ or methacrylic acid), with two $[TiO_6]$ octahedra condensed to a zigzag chain of two $[YO_8]$ dodecahedra and two $[TiO_6]$ octahedra, were formed when the Ti/Y ratio in the precursor mixture was ≥ 3.5. The structure of $Ti_4Y_2O_4(OMc)_{12}(OCH_2CH_2OMe)_2(McOH)_2$ obtained with a Ti/Y ratio of 2 in the precursor mixture, consists of a ring of four corner-sharing $[TiO_6]$ octahedra to which two $[YO_8]$ dodecahedra are condensed.

Introduction

The traditional sol-gel route to inorganic-organic hybrid polymers, in which the organic and inorganic entities are connected by covalent bonds, is based on molecular precursors of the general composition $(RO)_nM{-}X{-}A$ with a hydrolyzable group $(RO)_nM$, and a polymerizable organic group A connected by an inert spacer X. In a typical preparative protocol the precursors are first reacted with water. After formation of the inorganic network, the organic groups A are polymerized or crosslinked to form oligomeric or polymeric organic structures. Modification of the type, structure and proportions of the organic and inorganic constituents allows, in principle, tailoring of the properties of the resulting hybrid polymer. A special challenge of increasing importance is to tailor also structural features of the hybrid materials, especially the dimension (especially on a nanometer scale), geometry and mutual arrangement of the organic and inorganic building blocks.

Such a structural control is hardly possible with the traditional procedure. It is more easily reached when the formation of the inorganic and organic structures is done at different times in clearly separated reaction steps. Hydrolysis and condensation of metal or semi-metal alkoxides may lead to structurally defined molecular cage compounds (clusters), instead of oligomers or polymers with broad size distributions, if the reaction with water is performed in a very controlled manner. Such clusters can be used for the preparation of inorganic-organic hybrid polymers as structurally well-defined oligomeric building blocks. In order to connect the clusters with polymeric organic structures, the cluster surface must be covered with reactive organic groups (polymerizable groups, for example).

We previously synthesized a variety of methacrylate-substituted mono- (Ti, Zr, Hf, Nb, Ta), di- (Ti/Zr, Ti/Hf) and trimetallic (Ti/Zr/Hf) oxo/alkoxo clusters of different size and shape for this purpose.[1] It was shown that the cluster type has a distinct influence on the properties of the resulting hybrid materials;[2] the origin of this effect is not yet known. The methacrylate-substituted metal oxo clusters can be obtained in high yields by reaction of metal alkoxides with methacrylic acid (McOH). The formation of the clusters can be rationalized by the sequence of three reactions. One or more alkoxide ligands of the starting alkoxide $M(OR)_x$ are first substituted by methacrylate groups to give $M(OR)_{x-n}(OMc)_n$. Water is generated in situ by esterification of excess methacrylic acid with alcohol (either liberated by the substitution reaction or present as solvent)[3] and hydrolyzes all or part of the remaining alkoxide groups. The very slow in situ production of water allows a very controlled growth of clusters $M_nO_x(OR/OH)_y(OMc)_z$, the size and shape of which can be influenced to a certain degree by the reaction conditions. The most important parameter is the metal alkoxide/carboxylic acid ratio,[4] and a second parameter is the type of alkoxide group in the parent alkoxide.[5]

In this article we report the preparation of three methacrylate-substituted titanium-yttrium mixed-metal oxo clusters obtained by this route, viz. $Ti_4Y_2O_4(OMc)_{14}(MeOCH_2CH_2OH)_2$ (**1**), $Ti_4Y_2O_4(OMc)_{14}(McOH)_2$ (**2**) and $Ti_4Y_2O_4(OMc)_{12}(OCH_2CH_2OMe)_2(McOH)_2$ (**3**), and their structural characterization.

Results and Discussion

We have previously prepared a series of mixed Ti/Zr oxide clusters, viz. $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$ (Ti_2Zr_4),

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$Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$ (Ti_4Zr_2), $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ and $Ti_2Zr_6O_6(OMc)_{20}$, and related Ti/Hf and Ti/Zr/Hf clusters, by reacting titanium and zirconium (hafnium) butoxide mixtures with methacrylic acid in different molar ratios.[6,7] The same procedure was used in the present work to prepare Ti/Y clusters from Ti(O*n*Pr)$_4$ and $Y(OCH_2CH_2OMe)_3$. The latter alkoxide, with a decameric ring structure,[8] was employed as a ca. 11% solution in 2-methoxyethanol. The metal alkoxide [Ti(OR)$_4$ + Y(OME)$_3$]/methacrylic acid molar ratio (OME = OCH_2CH_2OMe)was kept at about 1:7 in each experiment, but the Ti(OR)$_4$/Y(OME)$_3$ ratio was varied from 2:1 to 3.5:1 and 18:1. Each precursor composition resulted in a different mixed-metal cluster **1−3** which was isolated in high yields in each case and structurally characterized by single crystal diffraction. The NMR spectra, both in benzene solution and in the solid state, are of little diagnostic value, because only one group of signals is observed for each type of ligand.

Interestingly, each of the clusters **1−3** has the general composition $Ti_4Y_2O_4X_{14}(HY)_2$ (X,Y = OMc and/or OME) despite the different Ti/Y ratio in the precursor mixture. The clusters differ by the distribution of X and Y, and by the arrangement of the titanium and yttrium polyhedra as discussed in the following.

Cluster **1** was obtained from a Ti(OR)$_4$/Y(OME)$_3$ ratio of 3.5. An X-ray structure analysis revealed that the composition of **1** is $Ti_4Y_2(\mu_3\text{-}O)_4(\mu_2\text{-}OMc)_{12}(\mu_1\text{-}OMc)_2(MeOCH_2CH_2OH)_2$. The structure of **1** (Figure 1, Table 1) is very similar to that of Ti_4Zr_2 [= $Ti_4Zr_2(\mu_3\text{-}O)_4(\mu_2\text{-}OMc)_{10}(\mu_2\text{-}OBu)_2(\mu_1\text{-}OBu)_2$] (Figure 2).

The common structural motive of the hexanuclear clusters Ti_2Zr_4 and Ti_4Zr_2 is a zigzag chain of two central [ZrO_8] dodecahedra and two terminal [TiO_6] tetrahedra. Two additional [ZrO_8] dodecahedra (in Ti_2Zr_4) or [TiO_6] octahedra (in Ti_4Zr_2) are condensed to the zirconium atoms of the main chain by a shared edge. The central structural motif of **1** is the same zigzag chain as in Ti_4Zr_2 with [YO_8] instead of [ZrO_8] dodecahedra. The main structural difference is that the additional [TiO_6] octahedra are condensed to the main chain via corners.

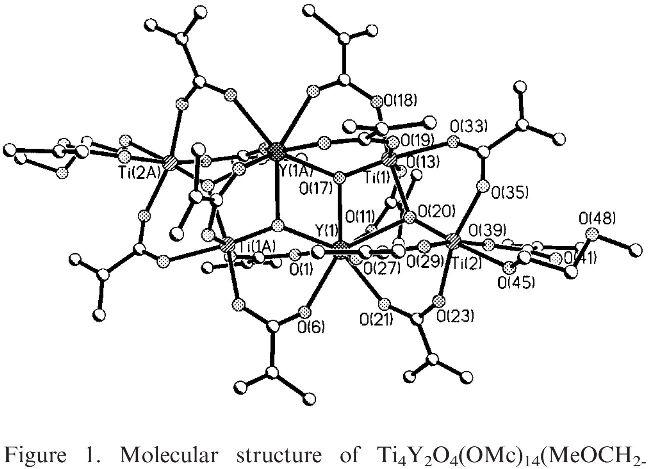

Figure 1. Molecular structure of $Ti_4Y_2O_4(OMc)_{14}(MeOCH_2CH_2OH)_2$ (**1**)

Table 1. Bond lengths [pm] and angles [deg] for **1** (* = − *x* + 1, −*y* + 1, −*z* + 1)

Y(1)−Ti(1)	333.59(6)	Ti(2)−O(35)	199.3(2)
Y(1)−Ti(1)*	372.62(6)	Ti(2)−O(39)	195.6(2)
Y(1)−Y(1)*	388.16(5)	Ti(2)−O(45)	218.0(2)
Ti(1)−O(13)	198.7(2)	Y(1)−O(1)	229.2(2)
Ti(1)−O(17)	171.9(2)	Y(1)−O(6)	235.4(2)
Ti(1)−O(18)	195.8(2)	Y(1)−O(11)	233.6(2)
Ti(1)−O(19)	201.1(2)	Y(1)−O(17)	233.0(2)
Ti(1)−O(20)	202.3(2)	Y(1)−O(17)*	235.8(2)
Ti(1)−O(33)	212.2(2)	Y(1)−O(20)	250.6(2)
Ti(2)−O(20)	173.4(2)	Y(1)−O(21)	231.6(2)
Ti(2)−O(23)	197.0(2)	Y(1)−O(27)	231.4(2)
Ti(2)−O(29)	198.8(2)		
O(1)−Y(1)−O(27)	148.73(7)	O(13)−Ti(1)−O(19)	165.95(9)
O(21)−Y(1)−O(17)	141.26(7)	O(18)−Ti(1)−O(20)	172.49(8)
O(27)−Y(1)−O(11)	139.52(7)	O(17)−Ti(1)−O(33)	172.38(9)
O(17)−Y(1)−O(6)	144.57(7)	O(23)−Ti(2)−O(35)	165.09(9)
O(11)−Y(1)−O(6)	130.69(7)	O(20)−Ti(2)−O(45)	174.45(9)
O(21)−Y(1)−O(17)*	149.25(7)	Ti(1)−O(17)−Y(1)	110.01(8)
O(11)−Y(1)−O(17)*	130.56(7)	Ti(1)−O(17)−Y(1)*	131.45(9)
O(1)−Y(1)−O(20)	140.29(6)	Y(1)−O(17)−Y(1)*	111.76(7)
O(6)−Y(1)−O(20)	137.31(7)	Ti(2)−O(20)−Ti(1)	136.96(11)
O(17)*−Y(1)−O(20)	121.42(6)	Ti(2)−O(20)−Y(1)	125.48(9)
		Ti(1)−O(20)−Y(1)	94.29(7)

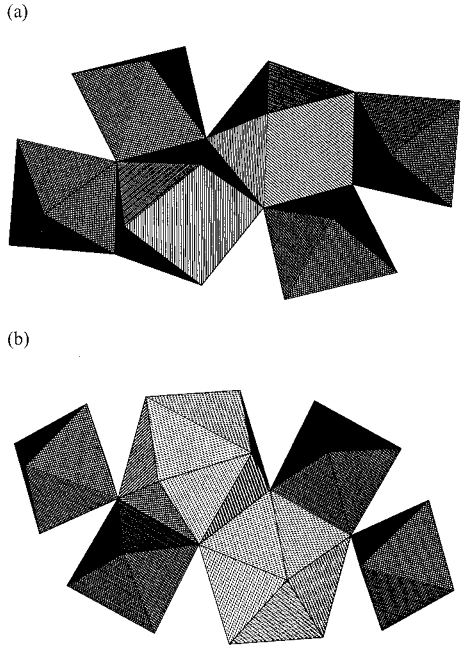

Figure 2. Cluster cores of connected polyhedra in $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$ (Ti_4Zr_2) (a) and **1/2** (b). The central polyhedra are eight-coordinate Zr or Y, and the terminal polyhedra six-coordinate Ti

While the sum of the metal coordination numbers in Ti_4Zr_2 and **1** is the same, the total metal charge in **1** is smaller by two units [Y^{III} instead of Zr^{IV}). That means that two of the 16 ligands in **1** must be neutral, i.e. must be coordinated in their protonated form. The protonated ligands are clearly identified by comparing the Ti−O and Y−O distances. The Ti−O distance associated with the OME group in **1** [Ti(2)−O(45) 218.0(2) pm] is much longer than comparable Ti−OR distances *trans* to a μ_3-oxo ligand [for example, Ti−OPr 180.3(2) in $Ti_3O(OPr)_9(OOCPh)_2$,[9] 179.3(3) in $Ti_6O_4(OEt)_8(OAc)_8$,[10] or 178.7(2) in $Ti_4O_2(OiPr)_6(OMc)_6$ [5]]. Thus, O(45) *trans* to the μ_3-oxo group at Ti(2) is the oxygen atom of a coordinated alcohol rather than an alkoxide ligand. The alcoholic hydrogen atom at O(45) undergoes an intramolecular hydrogen bond with the non-coordinated oxygen atom O(41) of the neighboring μ_1-OMc ligand [O(41)−O(45) 259.4 pm]. The presence of a weakly coordinating ROH ligand also manifests itself in the very short Ti(2)−O(20) distance [173.4(2) pm] [for comparison, Ti-μ_3-O distances *trans* to Ti−OR are 185.6(2) in $Ti_3O(OPr)_9(OOCPh)_2$, 209.9(1) in $Ti_6O_4(OEt)_8(OMc)_8$ and 208.9(2) in $Ti_4O_2(OiPr)_6(OMc)_6$].

A very similar cluster was obtained when the $Ti(OR)_4/Y(OME)_3$ ratio in the starting mixture was 18. The structure of **2** (Figure 2 and 3, Table 2) is basically the same as that of **1** with coordinated methacrylic acid molecules instead of the coordinated alcohols [i.e., $Ti_4Y_2(\mu_3\text{-}O)_4(\mu_2\text{-}OMc)_{12}(\mu_1\text{-}OMc)_2(McOH)_2$]. This can be rationalized by the smaller concentration of methoxyethanol in the starting mixture due to the low portion of $Y(OME)_3$ (which is employed as a solution in methoxyethanol).

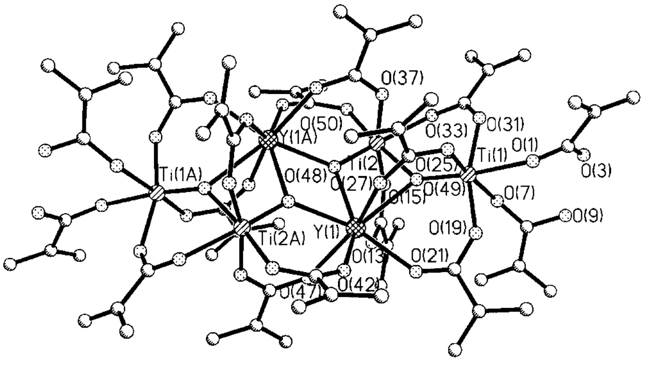

Figure 3. Molecular structure of $Ti_4Y_2O_4(OMc)_{14}(McOH)_2$ (**2**)

The coordinated methacrylic acid molecules are coordinated via the oxygen atom of their C=O double bond, while the OH hydrogen atom once again forms a hydrogen bond to the non-coordinated oxygen atom of the neighboring μ_1-OMc ligand [O(3)−O(9) 222.1(11) pm]. The Ti(1)−O(1) distance of the (neutral) methacrylic acid ligand [212.6(2) pm] is clearly longer than that of the (anionic) μ_1-methacrylate ligand [Ti(1)−O(7) 198.0(3) pm].

When the $Ti(OR)_4/Y(OME)_3$ ratio in the precursor mixture was lowered to 2, cluster **3** was obtained. The blueprint of **3** is completely different from that of **1** and **2**, although cluster **3** has the same overall composition as **1** (i.e. clusters **1** and **3** are geometric isomers). The neutral (protonated) ligand in **3** is McOH rather than $HOCH_2CH_2OMe$, as in **1**. This shift in protons results in dramatic structural changes. The structure (Figure 4, Table 3) consists of a ring of four corner-sharing $[TiO_6]$ octahedra to which two $[YO_8]$ dodecahedra are condensed (Figure 5). This arrangement of the polyhedra implies that only two of the oxo ligands are μ_3 [O(26)], while the other two oxo ligands are μ_2 [O(39)].

Table 2. Bond lengths [pm] and angles [deg] for **2** (*: $-x+1, -y, -z+1$)

Ti(2)−Y(1)	333.85(6)	Ti(2)−O(37)	201.1(2)
Y(1)−Y(1)*	386.35(6)	Ti(2)−O(49)	202.0(2)
Ti(1)−O(1)	212.6(2)	Ti(2)−O(50)	194.6(2)
Ti(1)−O(7)	198.0(3)	Y(1)−O(13)	234.6(2)
Ti(1)−O(19)	198.8(3)	Y(1)−O(21)	228.5(2)
Ti(1)−O(25)	197.4(3)	Y(1)−O(27)	231.3(2)
Ti(1)−O(31)	199.2(3)	Y(1)−O(42)	234.9(2)
Ti(1)−O(49)	173.3(2)	Y(1)−O(47)	228.3(2)
Ti(2)−O(48)	172.0(2)	Y(1)−O(48)	232.0(2)
Ti(2)−O(15)	199.0(3)	Y(1)−O(48)*	235.8(2)
Ti(2)−O(33)	212.7(2)	Y(1)−O(49)	255.1(2)
O(25)−Ti(1)−O(7)	169.58(11)	O(13)−Y(1)−O(48)*	127.15(8)
O(19)−Ti(1)−O(31)	163.52(11)	O(47)−Y(1)−O(49)	143.68(8)
O(49)−Ti(1)−O(1)	174.10(12)	O(42)−Y(1)−O(49)	132.29(8)
O(15)−Ti(2)−O(37)	166.86(10)	O(48)*−Y(1)−O(49)	123.39(7)
O(50)−Ti(2)−O(49)	172.21(10)	Ti(2)−O(48)−Y(1)	110.59(10)
O(48)−Ti(2)−O(33)	173.03(10)	Ti(2)−O(48)−Y(1)*	132.48(11)
O(47)−Y(1)−O(27)	147.33(9)	Y(1)−O(48)−Y(1)*	111.37(8)
O(21)−Y(1)−O(48)	140.14(8)	Ti(1)−O(49)−Ti(2)	137.10(13)
O(27)−Y(1)−O(13)	139.65(8)	Ti(1)−O(49)−Y(1)	125.80(11)
O(48)−Y(1)−O(42)	142.57(9)	Ti(2)−O(49)−Y(1)	93.10(8)
O(13)−Y(1)−O(42)	136.40(9)	C(43)*−O(50)−Ti(2)	130.5(2)
O(21)−Y(1)−O(48)*	149.29(8)		

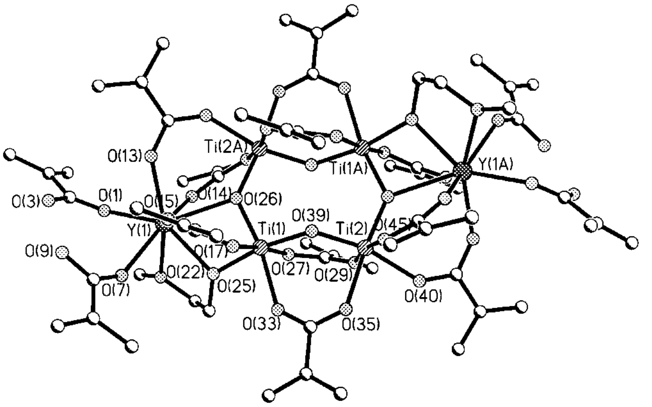

Figure 4. Molecular structure of $Ti_4Y_2O_4(OMc)_{12}(OCH_2CH_2OMe)_2(McOH)_2$ (**3**)

As in **2**, the neutral ligands are methacrylic acid molecules. However, in **3** both the monodentate OMc and HOMc ligands are bonded to the yttrium atoms. The methacrylic acid ligands are again coordinated via the oxygen atom of their C=O double bonds, and there is again a hydrogen bond between the OH hydrogen atom of the methacrylic acid and the non-coordinated oxygen atom of the neighboring μ_1-OMc ligand [O(3)−O(9) 240.8 pm].

Due to two oxo ligands now being μ_2 (rather than μ_3 as in **1** and **2**), each OCH_2CH_2OMe ligand in **3** must now occupy three coordination sites. In fact, the alkoxy oxygen atom [O(25)] bridges Ti(1) and Y(1), and the ether oxygen [O(22)] additionally coordinates to Y(1), thus **3** is $Ti_4Y_2(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OMc)_{10}(\mu_1\text{-}OMc)_2(\mu,\eta^2\text{-}OCH_2CH_2OMe)_2(McOH)_2$.

Table 3. Bond lengths [pm] and angles [deg] for **3** (*: $-x$, $-y$, $-z + 1$)

Ti(1)−Ti(2)	338.62(9)	Ti(2)−O(39)	178.1(2)
Y(1)−Ti(1)	338.20(7)	Ti(2)−O(40)	204.6(2)
Y(1)−O(26)	251.9(2)	Ti(2)−O(45)	196.9(3)
Ti(1)−O(17)	197.5(2)	Y(1)−O(1)	228.3(3)
Ti(1)−O(25	194.2(2)	Y(1)−O(7)	233.4(3)
Ti(1)−O(26)	184.4(2)	Y(1)−O(13)	223.9(3)
Ti(1)−O(27)	204.4(2)	Y(1)−O(14)	232.6(3)
Ti(1)−O(33)	208.2(2)	Y(1)−O(15)	235.4(3)
Ti(1)−O(39)	185.3(2)	Y(1)−O(22)	250.4(3)
Ti(2)−O(26)*	187.3(2)	Y(1)−O(25)	230.1(2)
Ti(2)−O(29)	203.3(3)	Y(1)−O(26)	251.9(2)
Ti(2)−O(35)	207.4(3)		
O(39)−Ti(1)−O(25)	169.27(10)	O(14)−Y(1)−O(15)	142.70(9)
O(17)−Ti(1)−O(27)	174.44(11)	O(13)−Y(1)−O(22)	146.33(10)
O(26)−Ti(1)−O(33)	168.72(10)	O(15)−Y(1)−O(22)	136.14(9)
O(45)−Ti(2)−O(29)	170.67(11)	O(1)−Y(1)−O(26)	148.76(11)
O(39)−Ti(2)−O(40)	165.55(11)	O(7)−Y(1)−O(26)	130.95(10)
O(26)*−Ti(2)−O(35)	173.84(10)	Ti(1)−O(26)−Ti(2)*	131.14(12)
O(13)−Y(1)−O(25)	142.15(9)	Ti(1)−O(26)−Y(1)	100.48(10)
O(1)−Y(1)−O(25)	141.37(10)	Ti(2)*−O(26)−Y(1)	126.29(11)
O(14)−Y(1)−O(7)	145.82(11)	Ti(2)−O(39)−Ti(1)	137.43(13)

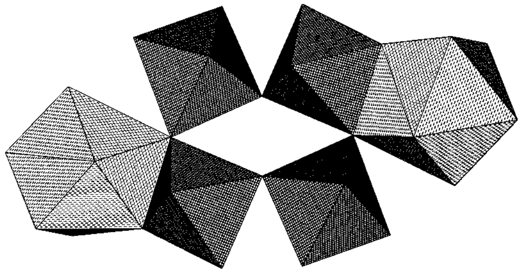

Figure 5. Cluster core of connected polyhedra in $Ti_4Y_2O_4(OMc)_{12}(OCH_2CH_2OMe)_2(McOH)_2$ (**3**). The central polyhedra are six-coordinate Ti and the terminal eight-coordinate Y.

Conclusions

Titanium-yttrium mixed-metal oxo clusters capped by polymerizable methacrylate ligands were prepared by reaction of mixtures of Ti(O*n*Pr)$_4$ and $Y(OCH_2CH_2OMe)_3$ with methacrylic acid. Only the ratio between the two alkoxides was varied while the metal alkoxide/methacrylic acid ratio was kept constant. This procedure resulted in two different cluster types. At a Ti/Y ratio of 2 in the precursor mixture, the cluster $Ti_4Y_2O_4(OMc)_{12}(OCH_2CH_2OMe)_2(McOH)_2$ (**3**) was formed with a ring of four corner-sharing [TiO_6] octahedra as the central structural motive to which two [YO_8] dodecahedra are condensed. At a Ti/Y ratio ≥ 3.5, clusters of the type $Ti_4Y_2O_4(OMc)_{14}L_2$ (**1**: L = $MeOCH_2CH_2OH$, **2**: L = McOH) were formed. The basic structural motive is a zigzag chain of two central [YO_8] dodecahedra and two terminal [TiO_6] octahedra to which two additional [TiO_6] octahedra are condensed. The second cluster type is very similar to the previously obtained titanium-zirconium mixed-metal clusters $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$ and $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$. The formation of the two different Ti/Y oxo clusters is difficult to rationalize in terms of reactivity of the two alkoxide precursors. It must be kept in mind, however, that the $Ti(OPr)_4$/$Y(OME)_3$ precursor combination is more complicated than in previous syntheses of methacrylate-substituted oxo clusters: (i) An alcoholic solvent was involved, since $Y(OME)_3$ was employed as a methoxyethanol solution. Thus, when the $Y(OME)_3$ proportion was varied, the amount of methoxyethanol was also varied. It is well-known that the use of 2-methoxyethoxy groups changes sol-gel reactions of metal alkoxides significantly due to the coordination ability of the ether oxygen. (ii) The alkoxide ligands of the two metal precursors were different, and alkoxide exchange reactions may occur prior to reaction with the acid and/or water.

Another noteworthy feature of the clusters **1**−**3** is the presence of monodentate carboxylate ligands and coordinated alcohol or acid molecules. Both types of ligands are always in a *cis* position at the same metal. This allows the formation of a hydrogen bond between the alcoholic or carboxylic OH group and the C=O group of the monodentate methacrylate ligand, which probably stabilizes this unusual ligand combination. A similar situation was previously observed in the clusters $Zr_6(OH)_4O_4(OOCR)_{12}$(*n*PrOH) (R = Ph, CMe=CH$_2$).[11] The question whether conversion of a bidentate carboxylate ligand to a monodentate ligand, with concomitant coordination of a neutral ligand to the opened coordination site, is connected with the reactivity of the clusters is currently under investigation.

Experimental Section

All operations were carried out in Schlenk tubes under argon. $Ti(OPr)_4$ (98% in propanol) and $Y(OCH_2CH_2OMe)_3$ (11% in methoxyethanol) were used as received.

$Ti_4Y_2O_4(OMc)_{14}(MeOCH_2CH_2OH)_2$ (1): An amount of methacrylic acid (1.02 g, 11.8 mmol) was added dropwise at room temperature to a stirred mixture of $Ti(OPr)_4$ (0.38 g, 1.32 mmol) (98% in propanol) and 0.39 mmol of $Y(OCH_2CH_2OMe)_3$ (1.11 g of a ca. 11% methoxyethanol solution). After 7 days at room temperature, 0.31 g of colorless crystals were formed (87% yield relative to Y). The crystals were separated and dried at in vacuo. $C_{62}H_{86}O_{36}Ti_4Y_2$ (1776.7): calcd. C 41.9, H 4.9, TiO_2/Y_2O_3 30.6; found C 42.1, H 4.6, TiO_2/Y_2O_3 32.8 (TGA). IR-ATR: $\tilde{\nu}$ = 2927 (w, CH), 1668 (w, C=C), 1566 (s, sh, COO), 1464 (s), 1424 (s), 1270 (s), 1129 (m), 1031 (m), 978 (m,$CH_{C=CH_2}$), 849 (m), 797 (m) cm^{-1}.

$Ti_4Y_2O_4(OMc)_{14}(McOH)_2$ (2): An amount of methacrylic acid (2.57 g, 29.9 mmol) was added dropwise at room temperature to a stirred mixture of $Ti(OPr)_4$ (1.11 g, 3.8 mmol) (98% in propanol) and 0.21 mmol of $Y(OCH_2CH_2OMe)_3$ (0.60 g of a ca. 11% methoxyethanol solution). After 8 days at room temperature, 0.23 g of colorless crystals were formed (quantitative yield relative to Y). The crystals were separated and dried at in vacuo. $C_{64}H_{82}O_{36}Ti_4Y_2$ (1796.7): calcd. C 42.8, H 4.6, TiO_2/Y_2O_3, 30.2; found C 41.6, H 4.7, TiO_2/Y_2O_3, 32.4 (TGA). IR-ATR: $\tilde{\nu}$ = 2927 (w, CH), 1642 (w, C=C), 1546 (s, sh, COO), 1454 (s), 1405 (s, sh), 1241 (s), 1112 (m), 1007 (m), 940 (m, $CH_{C=CH_2}$), 827 (m), 764 (m) cm^{-1}.

$Ti_4Y_2O_4(OMc)_{12}(OCH_2CH_2OMe)_2(McOH)_2$ (3): Methacrylic acid (0.74 g, 8.6 mmol) was added dropwise at room temperature to a

Table 4. Crystallographic and structural parameters of **1−3**

	1	**2**	**3**
Empirical formula	$C_{62}H_{86}O_{36}Ti_4Y_2$	$C_{64}H_{82}O_{36}Ti_4Y_2$	$C_{62}H_{86}O_{36}Ti_4Y_2$
Molecular mass	1776.7	1796.7	1776.7
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a [pm]	1136.6(1)	1145.83(7)	1117.1(1)
b [pm]	1283.3(1)	1249.25(8)	1366.1(2)
c [pm]	1493.2(1)	1448.52(9)	1409.2(2)
α [deg]	91.410(2)	84.884(1)	71.659(2)
β [deg]	103.669(2)	82.250(1)	75.690(2)
γ [deg]	110.698(2)	76.971(1)	76.208(2)
Volume [pm^3]	$1965.6(3)\cdot10^6$	$1997.9(2)\cdot10^6$	$1947.6(4)\cdot10^6$
Z/calcd. density [g·cm^{-3}]	1/1.492	1/1.493	1/1.513
μ [mm^{-1}]	1.932	1.902	1.950
Crystal size [mm]	0.42 × 0.31 × 0.23	0.30 × 0.24 × 0.18	0.39 × 0.23 × 0.19
2θ range	2.69−28.32	2.44−30.06	2.27−28.33
Reflections coll./unique	13838/9523	15837/11271	13818/9496
Data/parameters	9523/485	11271/479	9496/469
GOF	1.024	1.024	1.007
*R*1 [$I > 2\sigma(I)$]	0.0438	0.0572	0.0553
*wR*2	0.1090	0.1469	0.1357
Largest diff. peak and hole [e·Å^{-3}]	0.716/−0.315	1.024/−0.630	1.103/−0.452

stirred mixture of $Ti(OPr)_4$ (0.23 g, 0.8 mmol, 98% in propanol) and $Y(OCH_2CH_2OMe)_3$ (0.39 mmol, 1.13 g of a ca. 11% methoxyethanol solution). After 3 days at room temperature, 0.31 g of colorless crystals were formed (87% yield relative to Y). The crystals were separated and dried in vacuo. $C_{62}H_{86}O_{36}Ti_4Y_2$ (1776.7): calcd. C 41.9, H 4.9, TiO_2/Y_2O_3, 30.6; found C 41.9, H 4.7, TiO_2/Y_2O_3, 32.3 (TGA). IR-ATR: $\tilde{\nu}$ = 2926 (w, CH), 1644 (w, C=C), 1571 (s, COO), 1455 (s), 1387 (s, sh), 1369 (s), 1236 (s), 1103 (m), 1065 (m), 1006 (m), 938 (m, $CH_{C=CH_2}$), 826 (m), 736 (m) cm^{-1}.

X-ray Structure Analyses of 1−3: See also Tables 1−4. Selected crystals were mounted on a Bruker AXS SMART diffractometer with an APEX CCD area detector. Graphite-monochromated Mo-K_α radiation (71.073 pm) was used for all measurements. The crystal-to-detector distance was 5.00 cm. A hemisphere of data was collected by a combination of three sets of exposures at 173 K. Each set had a different φ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. The structure was solved by direct methods (SHELXS-86). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL-93) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. In **2**, O(48) is disordered and was refined with a 0.5:0.5 occupation of O(48) and O48(A). Crystallographic data (excluding structure factors) for the structures of **1−3** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-220753 (**1**), -220751 (**2**), -220752 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] Review articles: F. Ribot, C. Sanchez, *Comments, Inorg. Chem.* **1999**, *20*, 327. G. Kickelbick, U. Schubert, *Monatsh. Chem.* **2001**, *132*, 13. U. Schubert, *Chem. Mater.* **2001**, *13*, 3487. U. Schubert, *J. Sol-Gel Sci. Technol.,* in press.

[2] S. Gross, V. Di Noto, G. Kickelbick, U. Schubert, *Mat. Res. Soc., Symp. Proc.* **2002**, *726*, 47.

[3] G. Kickelbick, M. P. Feth, H. Bertagnolli, M. Puchberger, D. Holzinger, S. Gross, *J. Chem. Soc., Dalton* **2002**, 3892.

[4] B. Moraru, S. Gross, G. Kickelbick, G. Trimmel, U. Schubert, *Monatsh. Chem.* **2001**, *132*, 993.

[5] B. Moraru, N. Hüsing, G. Kickelbick, U. Schubert, P. Fratzl, H. Peterlik, *Chem. Mater.* **2002**, *14*, 2732.

[6] B. Moraru, G. Kickelbick, U. Schubert, *Eur. J. Inorg. Chem.* **2001**, 1295.

[7] S. Gross, G. Kickelbick, M. Puchberger, U. Schubert, *Monatsh. Chem.* **2003**, *134*, 1053.

[8] O. Poncelet, L. G. Hubert-Pfalzgraf, J. C. Daran, R. Astier, *J. Chem. Soc., Chem. Commun.* **1989**, 1846.

[9] I. Mijatovic, G. Kickelbick, M. Puchberger, U. Schubert, *New J. Chem.* **2003**, *27*, 3.

[10] I. Gautier-Luneau, A. Mosset, J. Galy, *Z. Kristallogr.* **1987**, *180*, 83.

[11] G. Kickelbick, P. Wiede, U. Schubert, *Inorg. Chim. Acta* **1999**, *284*, 1.

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