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Can the Clusters $Zr_6O_4(OH)_4(OOCR)_{12}$ and $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ Be Converted into Each Other?

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Upon reaction of zirconium alkoxides, $Zr(OR)_4$, with carboxylic acids, the clusters $Zr_6O_4(OH)_4(OOCR)_{12}$ (**Zr6**) or $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ (**Zr12**) were obtained, depending on the employed carboxylic acid. The structures of **Zr12** clusters with acetate, propionate, vinyl acetate or 3,3′-dimethylacrylate ligands were determined by single-crystal X-ray diffraction, as well as that of methacrylate/acetate and methacrylate/propionate mixed-ligand clusters. The structure of the hafnium cluster $[Hf_6O_4(OH)_4(acetate)_{12}]_2$ is also reported for comparison. The **Zr12** clusters are structurally related to the **Zr6** clusters since they are composed of two **Zr6** sub-units which are bridged by four carboxylate ligands. In each compound, carboxylic acid molecules interact with the cluster by hydrogen bonding to part of the μ_3-OH ligands. The clusters are highly dynamic in solution, due to site exchange of the carboxylate ligands; low-temperature NMR spectra of the clusters correspond to the solid-state structures. The **Zr6** and **Zr12** clusters can be clearly distinguished by their solution NMR spectra. Reactions between selected **Zr12** clusters and carboxylic acids led to the conclusion, that only part of the ligands is accessible for ligand exchange reactions. In contrast, all ligands were exchanged when the **Zr6** cluster $Zr_6O_4(OH)_4(methacrylate)_{12}$ was treated with an excess of propionic acid, and $Zr_6O_4(OH)_4(propionate)_{12}$ was formed. However, the **Zr12** cluster $[Zr_6O_4(OH)_4(propionate)_{12}]_2$ was obtained from the reaction of $Zr(OBu)_4$ with propionic acid. The **Zr6** and **Zr12** clusters thus do not interconvert at the given reaction conditions.

Introduction

We have previously prepared a variety of carboxylate-substituted titanium and zirconium oxo clusters, mainly to use the (meth)acrylate derivatives for the preparation of cluster-crosslinked polymers.[1] During this work, we obtained several types of zirconium oxo clusters, among them $Zr_6O_4(OH)_4(OOCR)_{12}$ (**Zr6**) and the dimer $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ (**Zr12**), having the same overall stoichiometry. Previous to this work, we obtained crystalline **Zr6** clusters for RCOO = methacrylate (**1**)[2] and 5-norbornene-2-carboxylate,[3] and the **Zr12** type for RCOO = acrylate.[4] The crystal structures of both cluster types additionally contain carboxylic acid molecules interacting with the ligand shell of the clusters by hydrogen bonding (see below).

The **Zr6** clusters consist of a $Zr_6O_4(OH)_4$ cluster core in which the triangular faces of a Zr_6 octahedron are alternatively capped by μ_3-O and μ_3-OH groups. The structure of the **Zr12** cluster consists of two **Zr6** sub-units which are connected by four carboxylate bridges. This will be discussed below in more detail. In a formal manner, the **Zr12** clusters can be constructed by opening two μ_2-(edge-bridging) carboxylate ligands of **Zr6** and letting two such units dimerize as shown in Figure 1.

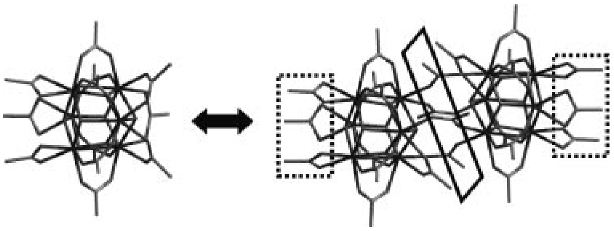

Figure 1. The schematic structures of **Zr6** [$Zr_6O_4(OH)_4(OOCR)_{12}$, left] and **Zr12** ([$Zr_6O_4(OH)_4(OOCR)_{12}]_2$, right) showing that the molecular structure of **Zr12** is derived from the **Zr6** structure. The dashed boxes mark the chelating ligands, and the box drawn with solid lines the carboxylate bridges connecting the Zr_6 sub-units.

The clusters were obtained when $Zr(OR')_4$ was treated with the corresponding carboxylic acid. In each case, only one cluster type was obtained, mostly in very high to quantitative yields, i.e. we never obtained mixtures of both clusters. This raises the question whether the formation of either cluster is controlled by the particular reaction conditions or by the different carboxylate ligands including the hydrogen-bonded carboxylic acid molecules. Differences in the electronic and/or steric properties could determine which cluster is formed. A related question of practical im-

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portance, is whether the **Zr6** and **Zr12** clusters can be converted into each other once they are formed. Since carboxylate-substituted metal alkoxides play an important role in sol-gel chemistry,[1,5] the conversion of intra-cluster bridges to inter-cluster bridges could result in the formation of oligomers or polymers made of cluster units, which could severely influence the structure of the networks formed during sol-gel processing.

We report in this article experiments proving that the two cluster types are not interconverted under the conditions employed during their synthesis. First, we will describe new **Zr12** clusters with different carboxylate ligands than previously described. Second, we will demonstrate that the **Zr6** and **Zr12** clusters can be clearly distinguished in solution by their NMR spectra. Third, we will show that each cluster type is retained when the ligands are exchanged; this renders possible the preparation of **Zr6** and **Zr12** clusters with the same ligands.

Results and Discussion

Preparation and Structures of New Zr12 Clusters

Cluster **1** was previously prepared by reaction of $Zr(OPr)_4$ in propanol or $Zr(OBu)_4$ in butanol with four equivalents of methacrylic acid.[2] The reported procedure is very reliable, and it is possible to prepare large quantities of this cluster per run for materials syntheses.[1] However, minor changes in the kind of employed carboxylic acid resulted in the formation of **Zr12** clusters instead. The crystalline clusters $[Zr_6O_4(OH)_4(OOCMe)_{12}]_2{\cdot}6MeCOOH{\cdot}3.5CH_2Cl_2$ (**2**), $[Zr_6O_4(OH)_4(OOCCH_2Me)_{12}]_2{\cdot}6MeCH_2COOH$ (**3**), $[Zr_6O_4(OH)_4(OOCCH_2CH{=}CH_2)_{12}]_2{\cdot}6CH_2{=}CHCH_2COOH$ (**4**) and $[Zr_6O_4(OH)_4(OOCCH{=}CMe_2)_{12}]_2{\cdot}4Me_2C{=}CHCOOH$ (**5**) were formed in high yields when an 80% solution of $Zr(OBu)_4$ in *n*-butanol was treated with acetic acid (10 molar equivalents), propionic acid (2–10 molar equivalents), vinylacetic acid (7 molar equivalents) or 3,3′-dimethylacrylic acid (4 molar equivalents), respectively. Methylene chloride was used as a co-solvent in the reaction of acetic acid to obtain crystals suitable for single crystal measurements. These reactions show that the **Zr12** cluster type is obviously obtained with a much broader range of carboxylic acids than the **Zr6** cluster type.

We have previously shown that the carboxylate ligands of the **Zr6** clusters can be partially or fully exchanged, when the **Zr6** clusters are reacted with a carboxylic acid. Partial exchange resulted in mixed-ligand clusters, which can alternatively be prepared by reaction of the metal alkoxide with mixtures of two carboxylic acids.[8,6] Mixed-ligand **Zr12** clusters can also be obtained by both methods. Crystalline $[Zr_6O_4(OH)_4(OOCCH_2Me)_3\{OOCC(Me){=}CH_2\}_9]_2{\cdot}CH_2{=}C(Me)COOH{\cdot}5MeCH_2COOH$ (**6**) was obtained by reaction of $Zr(OBu)_4$ with a 2:5 or 1:6 mixture of propionic and methacrylic acid, and $[Zr_6O_4(OH)_4(OOCMe)_8\{OOCC(Me){=}CH_2\}_4]_2{\cdot}6MeCOOH$ (**7**) by reacting $Zr(OBu)_4$ with five equivalents of a 1.4:3.6 mixture of methacrylic acid and acetic acid.

The cluster $[Hf_6O_4(OH)_4(OOCMe)_{12}]_2{\cdot}6MeCOOH{\cdot}6CH_2Cl_2$ (**8**) was similarly prepared by reaction of $Hf(OBu)_4$ with 10 molar equivalents of acetic acid in CH_2Cl_2. This **Hf12** cluster is isostructural to the zirconium cluster **2** and is therefore included in the discussion.

The solid-state structures of the **Zr12** clusters are fairly similar; differences are only observed for the carboxylic acids which are hydrogen-bonded to the cluster. We will therefore first discuss the structure of the vinyl acetate-substituted cluster **4** (Figure 2) as an example before we turn to the mixed-ligand clusters and point out differences among the different **Zr12** clusters.

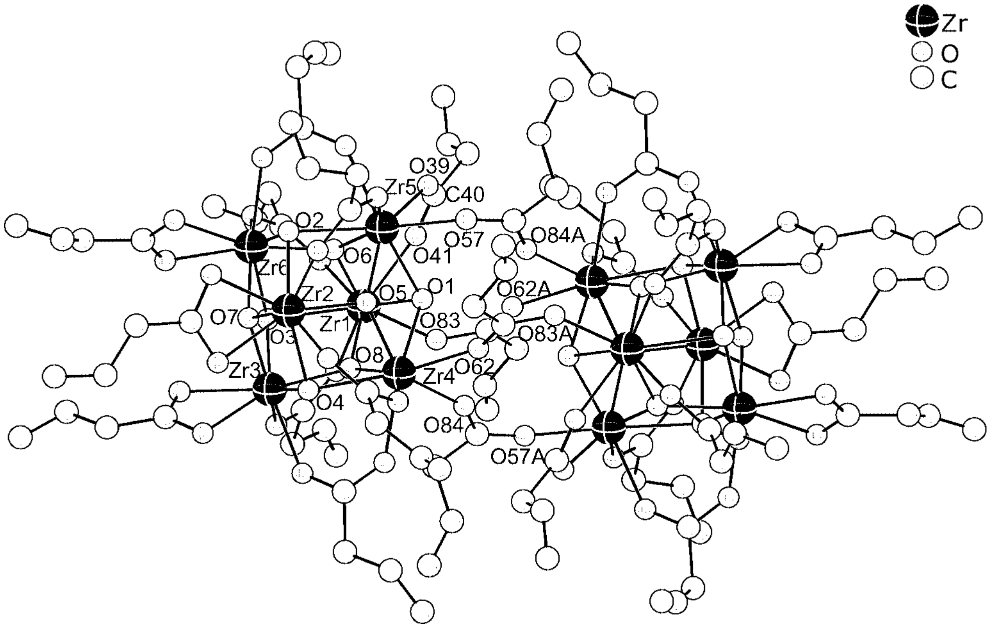

Figure 2. Structure of $[Zr_6O_4(OH)_4(OOCCH_2CH{=}CH_2)_{12}]_2$ (**4**).

The structure of **Zr6** (Figure 1, left) consists of a $Zr_6O_4(OH)_4$ core in which the triangular faces of a Zr_6 octahedron are alternatively capped by μ_3-O and μ_3-OH groups. The same cluster core was found in $Ce_6(OH)_4O_4$(acetylacetonate)$_{12}$.[7] Three carboxylate ligands of **Zr6** chelate the zirconium atoms at one μ_3-O capped face ("chelated face"), while the other nine OOCR groups bridge all edges of the Zr_6 octahedron except the edges of the chelated face. Each zirconium atom is coordinated by eight oxygen atoms. The cluster core thus has a C_{3v} symmetry with the C_3 axis passing through the center of the chelated face and the triangular face opposite to it.

The basic structural features of **Zr6** are retained in the sub-units of centrosymmetric **4** and all the other clusters of the **Zr12** type (Figure 1, right and Figure 2). The carboxylate ligands opposite the chelated face in the **Zr6** unit appear to be somewhat activated. For example, we previously obtained modifications of the **Zr6** structure, where *one* carboxylate ligand opposite the chelated face was opened to a monodendate coordination and the vacated coordination site occupied by a coordinated alcohol or a water molecule $[Zr_6O_4(OH)_4(OOCR)_{12}\cdot XOH$, X = R, H].[4,8] In **Zr12**, *two* of the bridging carboxylate ligands per Zr_6 unit opposite the chelated face are opened and are converted to inter-cluster bridges, i.e. the **Zr12** clusters are thus dimers of **Zr6** in which Zr_6 sub-units are connected by four inter-cluster carboxylate bridges. The third bridging carboxylate ligand opposite the chelated face [O(39)/C(40)/O(41)] stays bridging. This change of the coordination mode of two carboxylate units per Zr_6 unit from edge-bridging to inter-cluster bridging has only little effect on the geometrical parameters of the cores of the Zr_6 sub-units and the remaining carboxylate ligands.

The μ_3-O and μ_3-OH groups capping the Zr_6 core can be easily distinguished by their Zr–O distances. In **4**, the oxygen atoms O(5)–O(8) were μ_3-O (Zr–O distances between 203.5(2) and 210.7(2) pm, where the Zr–O distances at the chelated face were slightly longer [209.0–210.7 pm]), while O(1)–O(4) were μ_3-OH. While the Zr–O(1) distances (the μ_3-OH group opposite the chelated face) were quite uniform [229.8(2)–233.1(2) pm], that of the other three capping OH groups showed a pattern of two short [218.3(2)–221.7(2) pm] and one long [233.1(2)–239.1(2) pm] Zr–O distance, i.e. the groups are in fact between μ_2 and μ_3.

The Zr–O distances of the intra-cluster bridging carboxylate ligands (218.3–223.6 pm) in **4** were in the same range as the inter-cluster bridging ligands (216.6–222.3 pm) while the distances of the chelating ligands were distinctly longer. Remarkably, each chelating carboxylate ligand had a longer [229.7(2)–230.8(2) pm] and a significantly shorter [225.3(2)–227.4(2) pm] Zr–O bond length, which is due to the hydrogen bonds described below, the *shorter* distance being the oxygen atom interacting with the hydrogen-bonded acid.

The crystal lattice of **4** contains three vinylacetic acid molecules per asymmetric unit, which interact with the cluster subunits via hydrogen bridges. The OH group of each carboxylic acid is hydrogen-bonded to an oxygen atom of a *chelating* vinyl acetate ligand [O(9)···O(87) 265.8 pm, O(15)···O(93) 262.9 pm, O(23)···O(99) 263.8 pm] and the carbonyl oxygen of each carboxylic acid is hydrogen-bonded to one of the three μ_3-OH groups surrounding the chelating face [O(2)···O(85) 271.8 pm, O(3)···O(91) 275.0 pm, O(4)···O(97) 273.1 pm]. The hydrogen-bonding pattern in **4** is schematically shown in Figure 3.

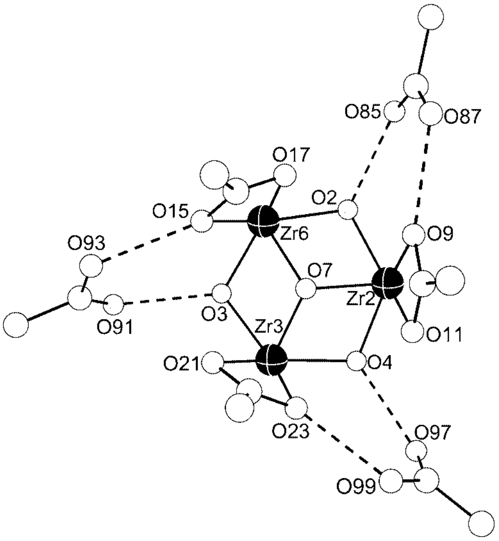

Figure 3. Hydrogen bonding patterns in **4**. The vinyl groups are omitted for clarity.

The hydrogen-bonding pattern of **4** (similar for the other **Zr12** clusters) is remarkable, as it shows that the μ_3-OH groups in the clusters are efficient proton donors in hydrogen bonds and thus enable the coordination of carboxylic acid molecules at the periphery of the clusters. This may be important for carboxylate-exchange reactions as discussed below (see also ref.[8]). As we have already pointed out in a related case,[9] the simultaneous action of carboxylic acids as hydrogen donors *and* hydrogen acceptors may stabilize unusual bonding situations.

The inorganic core of the mixed-ligand clusters **6** and **7** was the same as that of the other **Zr12** clusters, but the distribution of the ligands needs to be discussed. In the following discussion we distinguish between (i) the chelating ligands, (ii) the ligands bonded to zirconium atoms at the face of the Zr_6 octahedron opposite the chelated face ("opposite ligands"), which are the carboxylate bridges connecting the Zr_6 sub-units and the remaining edge-bridging ligand at the "opposite" face, and (iii) the ligands bridging the zirconium atoms of the "chelated" face and the "opposite" face ("belt ligands", see Figure 1). Cluster **6** is again centrosymmetric and contains three propionate and nine methacrylate ligands per Zr_6 sub-unit. All propionate groups were "opposite" ligands (Figure 4). In the acetate/methacrylate-substituted cluster **7**, with a lower proportion of methacrylate ligands, the saturated (acetate) ligands occupied again the "opposite" ligand positions and in addition part of the "belt" positions, while the methacrylate ligands were at the chelating and part of the "belt" positions (as a matter of fact, part of the belt positions contained disordered acetate and methacrylate ligands in the

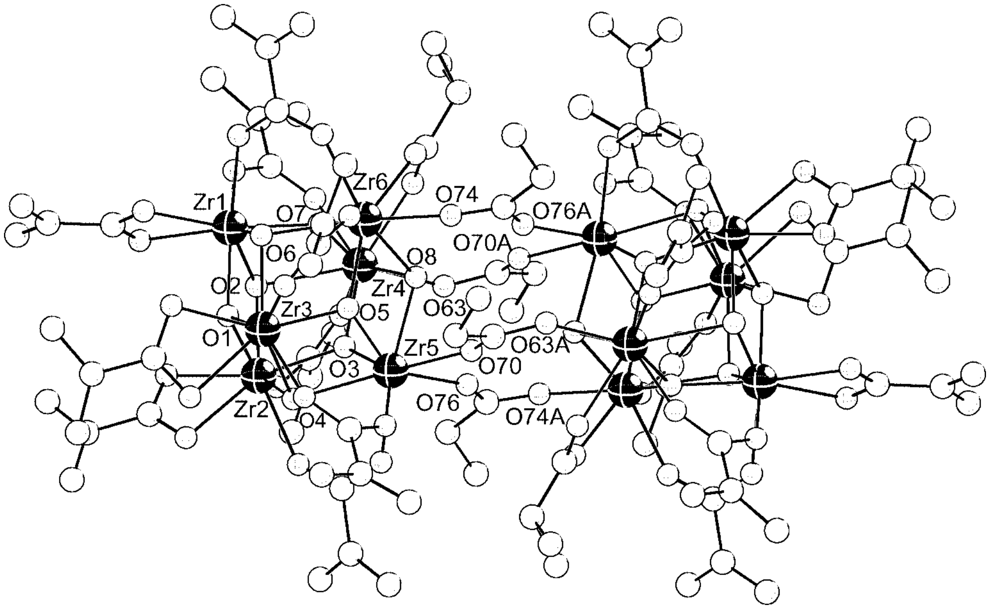

Figure 4. Structure of $[Zr_6O_4(OH)_4(OOCCH_2Me)_3\{OOCC(Me){=}CH_2\}_9]_2$ (**6**).

solid-state structure). There is obviously a clear preference of the methacrylate ligands in the order chelating > belt > opposite. The reason for this preference is currently speculative. One possibility is that the pK_a of methacrylic acid is slightly lower (4.66) than that of propionic acid (4.88) and acetic acid (4.76), and the site preference is thus due to the basicity of the anions. Another reason could be the slightly different steric demand of the ligands.

The molecular structures of all **Zr12/Hf12** clusters were essentially the same. However, different hydrogen-bonding patterns of the carboxylic acids were observed. In the clusters **2** and **8**, the hydrogen bonding was the same as in **4** discussed above. A second type of hydrogen bonding pattern was observed in **3**, **6** and **7**. Again, three carboxylic acid molecules are hydrogen-bonded per Zr_6 unit with the μ_3-OH groups neighboring the chelated face as the hydrogen donors to the carbonyl oxygen atoms. However, the OH groups of the carboxylic acid molecules interact in a different manner with the chelating ligands. In **6**, two carboxylic acid molecules interact with the two oxygen atoms of *one* chelating ligand. The second chelating ligand is hydrogen-bonded as in **4**, while the third is not involved in hydrogen bonding. The structure of **3** contained two half **Zr12** molecules in the asymmetric unit. One of them had the same hydrogen-bonding pattern as in **4**, and the other as in **6**. In **7**, the OH group of one acetic acid molecule interacted with *two* chelating carboxylate ligands (with rather long O···O interactions, 286–301 pm), the second oxygen atom of which was hydrogen-bonded to the other acetic acid molecules. The dimethylacrylate derivative **5** had only four hydrogen-bonded acid molecules, probably because of their greater steric bulk. One of the dimethylacrylic acid molecules is hydrogen-bonded as described above, i.e. the carbonyl oxygen interacts with one of the μ_3-OH groups [O(1)] and an oxygen of a chelating carboxylate ligand [O(30)]. The carbonyl group of the second hydrogen-bonded dimethylacrylic acid molecule interacts with the μ_3-OH group O(3), but the hydrogen atom of the carboxylic OH group interacts in a bifurcated manner with one oxygen atom of both other chelating carboxylate ligands.

NMR Spectra of Zr6 and Zr12 Clusters

For the NMR spectroscopic investigation of the clusters, the solvate molecules of the crystalline compounds were nearly completely removed by repeated dissolution/evaporation cycles, as described in the Experimental Section. We have previously reported the ^{1}H and ^{13}C NMR spectroscopic data of **1**,[8] where the signals in the room temperature spectra can be clearly assigned to three nonequivalent ligand positions (one chelating and two different bridging positions) according to the C_{3v} symmetry of the cluster in the crystalline state. The signal ratio of the olefinic CH_2 protons should therefore be 2:1:1, which was approximately found by integrating the corresponding signals of the solution ^{1}H NMR spectrum; the proton signals of all methyl groups were overlapping. The three different ligands can be easily distinguished in the $^{1}H/^{13}C$ HMBC spectrum of **1** (Figure 5), where long-range correlations between the olefinic CH_2 and CH_3 protons to the corresponding carboxylate carbon atoms were observed. The signals at δ = 6.10/5.65 ppm (^{1}H NMR) and 184.7 ppm (^{13}C NMR) were therefore assigned to the chelating ligands, and those at 5.97/5.39 ppm (^{1}H NMR) and 171.9 ppm (^{13}C NMR) as well as those at 6.04/5.60 ppm (^{1}H NMR) and 169.6 ppm (^{13}C NMR) to the two inequivalent bridging ligands. This sequence of chemical shifts shows that ^{13}C NMR signals of chelating carboxylates are distinctly shifted to a lower field.

This is in line with previous work on zinc carboxylate clusters, where this was explained by electronic effects of the bound metal(s).[10]

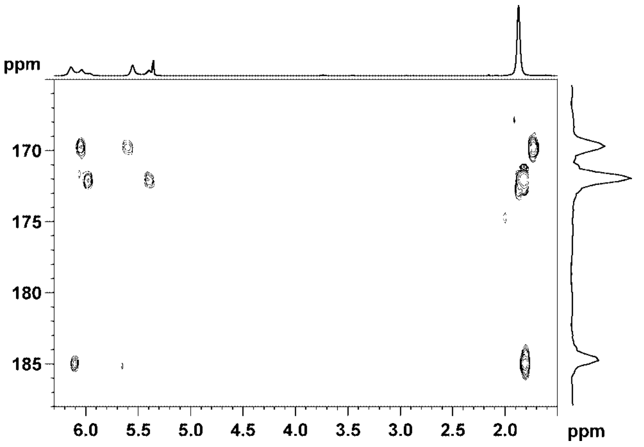

Figure 5. $^1H/^{13}C$ HMBC spectrum of **1** at room temperature in CD_2Cl_2.

We start the discussion of the NMR spectra of the **Zr12/Hf12** clusters with the simpler cases, i.e. the acetate-substituted clusters $[Zr_6O_4(OH)_4(OOCMe)_{12}]_2$ (**2**) and $[Hf_6O_4(OH)_4(OOCMe)_{12}]_2$ (**8**), which both show the same features in the NMR spectra. Six of the 24 acetate ligands are chelating ligands, 14 are bridging ligands within the same Zr_6 sub-unit and four ligands are inter-cluster bridging. The symmetry of the cluster in the crystalline state is C_i with 12 inequivalent ligand positions. Neglecting a slight perturbation of the symmetry by crystal packing or slightly different conformations of the acetate ligands, the molecular symmetry is in fact C_{2h} (Figure 6 (a)]. This results in seven nonequivalent ligand positions, i.e. two chelating, four bridging and one inter-cluster bridging, with a signal ratio of 1:1:2:2:2:2:2. In the case of a C_i symmetry three of the 12 ligand positions are chelating, seven are bridging and two are inter-cluster bridging. Their signal intensity should be the same. A comparison of these two cases is shown in Figure 6. In passing, it should be pointed out that, in the worst case for NMR investigations, all ligands may become inequivalent due to different ligand conformations. This may lead to different isomers and an even greater number of signals or broader resonances.

Temperature-dependent ^1H NMR spectra of solvate-free $[Zr_6O_4(OH)_4(OOCMe)_{12}]_2$ (**2**) in CD_2Cl_2 are shown in Figure 7. Five separated methyl signals were observed at 20 °C. Upon cooling the solution to –40 °C two additional signals appeared; the seven nonequivalent ligand signals in an approximate ratio of 1:1:2:2:2:2:2 indicate that the cluster has indeed C_{2h} symmetry in solution.

A tentative assignment of the signals was reached from a $^1H/^{13}C$ HMBC spectrum (Figure 8) and by comparison of the chemical shifts with those of compound **1**. The signal at δ = 1.75 ppm, which shows a long-range correlation to the most down-field shifted carboxylate at δ = 181.1 ppm, was assigned to a chelating acetate ligand, whereas the signal at δ = 2.05 ppm, showing a long-range correlation to

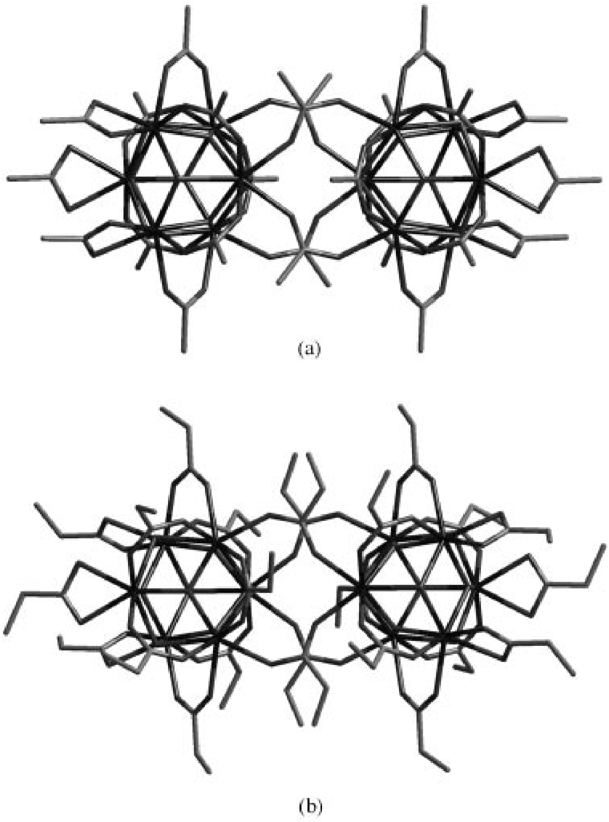

Figure 6. $[M_6O_4(OH)_4(OOCMe)_{12}]_2$ [M = Zr (**2**) or Hf (**8**); (a)] has a mirror plane whereas $[Zr_6O_4(OH)_4(OOCCH_2Me)_{12}]_2$ [**3**; (b)] only has an inversion center due to the different conformation of the ethyl groups.

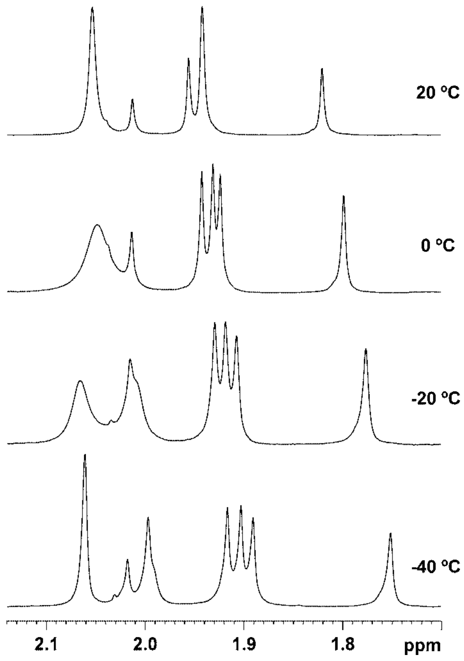

Figure 7. Temperature-dependent ^1H NMR spectra of $[Zr_6O_4(OH)_4(OOCMe)_{12}]_2$ (**2**) in CD_2Cl_2.

the most high-field shifted carboxylate at δ = 175.9 ppm, should correspond to a bridging ligand. The signals with long-range correlations between 2.02 ppm (^{1}H) and 176.6 ppm (^{13}C) as well as 2.00 ppm (^{1}H) and 176.6 ppm (^{13}C) appear in the ^{1}H NMR spectrum only with 50% intensity and can therefore be assigned to the set of intercluster bridging ligands and to the set of chelating ligands. The remaining three signals at 1.91 (δ = 177.4 ppm), 1.90 (δ =177.3 ppm) and 1.89 (δ = 177.5 ppm) must then be signals of the other bridging acetate ligands. The carbon signals of the methyl groups are listed in the Experimental Section.

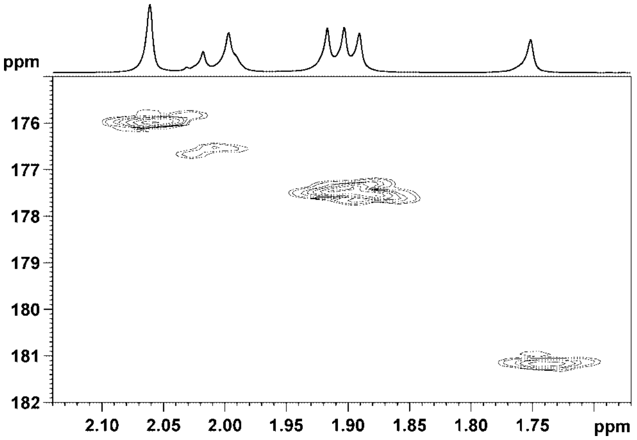

Figure 8. $^{1}H/^{13}C$ HMBC spectrum of **2** at –40 °C in CD_2Cl_2.

A different picture was obtained for the propionate-substituted cluster $[Zr_6O_4(OH)_4(OOCCH_2Me)_{12}]_2$ (**3**) in $[D_8]$-toluene (Figure 9). The ^{1}H NMR spectrum at room temperature showed sharp lines, and signals for six different ligands were observed. Five of them showed long-range correlations to carboxylate carbon atoms at 184.0, 179.9, 179.8, 179.7 and 178.4 ppm in a $^{1}H/^{13}C$ HMBC spectrum, whereas no long-range correlation was observed for the broad CH_3 signal at δ = 1.02 ppm. This is common for fast exchanging ligands in such cluster compounds.

Cooling the sample to –40 °C changed the picture, and signals for at least ten inequivalent ligands were observed in the ^{1}H NMR spectrum (not shown). This means that the symmetry of **3** is reduced to at least C_i or even C_1 at lower temperatures. In the $^{1}H/^{13}C$ HMBC spectrum at this temperature, six carboxylate signals were now resolved, and the signal, which formerly gave no long-range correlation, was shifted from 1.02 to 0.89 ppm and split into two proton signals, both of which gave a long-range correlation to the same carbon at δ = 192.0 ppm. This signal was also tentatively assigned to a chelating ligand. When the sample was further cooled to –80 °C (not shown) the lines in the spectrum became broad and unstructured. This indicated that at room temperature the symmetry is approximately C_{2h} because the ligand conformations are averaged on the NMR time scale. At lower temperature, the ligand motion is restricted, and the symmetry of the cluster is thus lowered, resulting in a larger number of signals.

These examples show that the **Zr6** and **Zr12** clusters can be clearly distinguished by their molecular symmetry and therefore by their NMR spectra in solution. While the C_{3v} symmetric **Zr6** cluster **1** has three sets of nonequivalent carboxylate ligands, the **Zr12** clusters have either C_{2h} or C_i symmetry and should therefore have either seven or 12 nonequivalent ligands. The symmetry of the cluster may even be reduced to C_1 and therefore the number of signals in the NMR spectra increases when the ligand motion is restricted. The NMR spectrum of **1** at room temperature had already shown signals for all three nonequivalent ligands (Figure 5). In the case of the **Zr12** clusters **2** and **3**, the room temperature NMR spectra show signals for five or six nonequivalent ligands, respectively. This indicates that site exchange of the ligands in **2** and **3** is much easier than that in the **Zr6** cluster **1**. Furthermore, it was observed that in the case of **3** the most dynamic region in this **Zr12** cluster is that of the chelating ligands.

It is worth noting at this point that the ability to distinguish clearly between a **Zr6** and a **Zr12** cluster is already a clear indication that there is no equilibrium between these two different clusters at room temperature in solution.

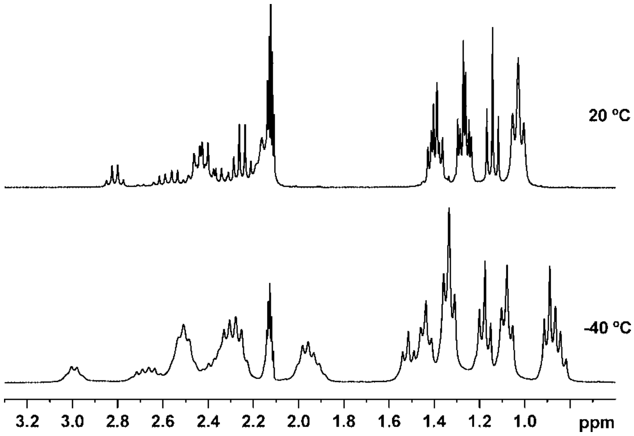

Figure 9. Temperature-dependent ^{1}H NMR spectra of $[Zr_6O_4(OH)_4(OOCCH_2Me)_{12}]_2$ (**3**) in $[D_8]$toluene.

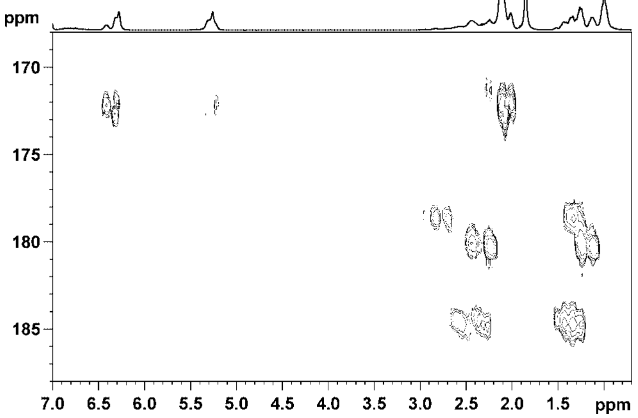

Figure 10. $^{1}H/^{13}C$ HMBC spectrum of $[Zr_6O_4(OH)_4(OOCCH_2Me)_3\{OOCC(Me)=CH_2\}_9]_2$ (**6**) at room temperature in $[D_8]$toluene.

To explore the ability of the **Zr12** clusters to undergo ligand exchange reactions and to compare this with the already known exchange behavior of the **Zr6** clusters[8,6] we analyzed the mixed propionate-methacrylate cluster **6**. The ^{1}H NMR spectrum of **6** in [D$_8$]toluene at room temperature showed broad and unstructured lines, due to ligand exchange. The corresponding ^{1}H/^{13}C HMBC spectrum (Figure 10) of **6** showed signals for only three different methacrylate ligands and six different propionate ligands. The carboxylate carbons of the methacrylate groups appeared at 171.5, 172.0 and 172.5 ppm, and that of the propionate ligands at 178.3, 178.4, 179.7, 179.8, 184.1 and 184.2 ppm.

Reaction of $[Zr_6O_4(OH)_4(OOCCH_2Me)_3\{OOCC(Me)=CH_2\}_9]_2$ (6) and $Zr_6O_4(OH)_4\{OOCC(Me)=CH_2\}_{12}$ (1) with Propionic Acid

Cluster **6** was treated with a large excess of propionic acid in CH_2Cl_2. After careful workup of the reaction product and excessive drying in vacuo, the ^{1}H NMR spectra (Figure 11) showed a complete exchange of the cluster-bonded methacrylate ligands against propionate ligands. The obtained spectrum is very similar to that of **3** directly prepared from $Zr(OBu)_4$ and propionic acid (see above). This indicated that in **Zr12** clusters at least the "outer" parts of the cluster, to which the 18 methacrylate ligands are bonded, are accessible to ligand exchange in solution.

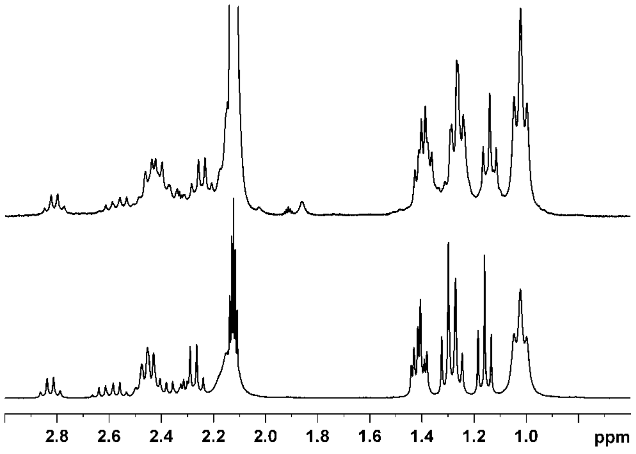

Figure 11. Top: ^{1}H NMR spectrum (in [D$_8$]toluene) of the reaction product of **6** with an excess of propionic acid in [D$_8$]toluene at room temperature. Bottom: ^{1}H NMR spectrum of solvate-free **3** for comparison.

To check whether all ligands can be exchanged, we used the propionate-substituted cluster **3**. Treatment with an excess of acetic acid should yield the acetate cluster $[Zr_6O_4(OH)_4(OOCMe)_{12}]_2$ (**2**) when all ligands are exchanged. The ^{1}H NMR spectrum of the reaction product is compared in Figure 12 (center) with the starting compound **3** (top) and **2** (bottom). It is easy to see that even after excessive treatment with acetic acids signals from propionate ligands were retained. The integration of the signals showed that the ratio of acetate to propionate was 3:1. This leads to the conclusion, that the "opposite ligands" of the **Zr12** cluster are not accessible for ligand exchange reactions in solution.

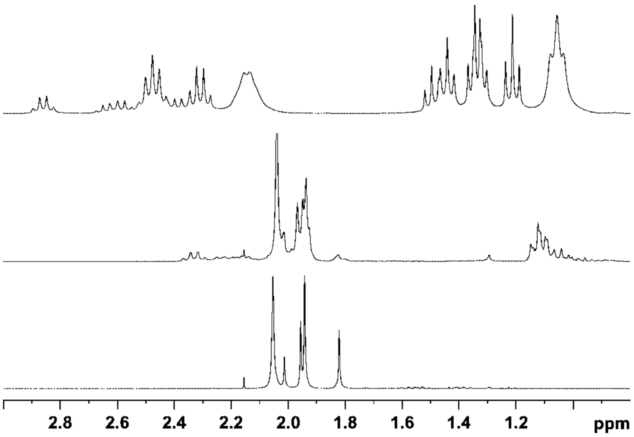

Figure 12. Top: ^{1}H NMR spectrum of $[Zr_6O_4(OH)_4(OOCCH_2Me)_{12}]_2$ (**3**). Bottom: ^{1}H NMR spectrum of $[Zr_6O_4(OH)_4(OOCMe)_{12}]_2$ (**2**), the expected reaction product. Center: Reaction product of **3** with an excess of acetic acid. All spectra were recorded at room temperature in CD_2Cl_2.

In contrast, when the **Zr6** cluster **1** was treated with a large excess of propionic acid, the NMR spectra clearly showed that no methacrylate ligands were left and therefore all ligands were exchanged against propionate.[8] In the ^{1}H/^{13}C HMBC spectrum of the reaction product (Figure 13), long-range correlations between the CH_2 and CH_3 protons of three different propionate groups to the corresponding carboxylate carbon atoms were observed. A comparison with the ^{1}H/^{13}C HMBC spectrum of **1** (Figure 5) showed a similar peak pattern of the signals; two of the signals appeared at a higher field (180.0 and 180.4 ppm), whereas one signal was shifted to lower field (δ = 184.0 ppm). The intensity ratio of the protons is also approximately 2:1:1 as found for **1**. This indicates strongly that the cluster core of the **Zr6** cluster was preserved during the exchange reaction, that the overall symmetry C_{3v} was retained and that $Zr_6O_4(OH)_4(propionate)_{12}$ was formed.

One of the key steps in the formation of zirconium oxo clusters from $Zr(OR')_4$ and carboxylic acids is the esterification reaction of the acid with the cleaved alcohol.[11] The thus-generated water is the source of the oxo and hydroxo ligands in the clusters. When mixed-ligand clusters are prepared from two different acids, the question is whether two esters were formed or just one. We therefore also monitored the formation of **6** in solution starting from $Zr(OBu)_4$ and a mixture of propionic and methacrylic acid by NMR spectroscopy, concentrating on signals from either butyl propionate or butyl methacrylate. After 6 h, the reaction was almost complete and no more ester was formed. The TOCSY spectrum (Figure 14, top) showed that the sharp triplet at δ = 3.93 ppm (marked by an arrow) can be assigned to the CH_2O moiety of a butyl residue, and the ^{1}H/^{13}C HMBC spectrum (Figure 14, bottom) shows a long-range correlation from this triplet to a propionate group at δ = 173.7 ppm. The other signals in the ^{1}H/^{13}C HMBC spec-

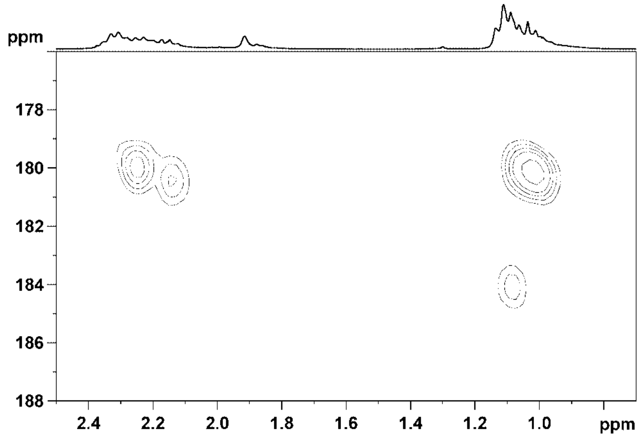

Figure 13. ^{1}H/^{13}C HMBC spectrum of the reaction product of **1** treated with an excess of propionic acid at room temperature in [D$_8$]toluene.

trum were due to methacrylic acid (δ = 173.0 ppm) and propionic acid (δ = 179.8 ppm). No butyl-methacrylate was formed during the reaction. This experiment shows that the formation rate of ester, and thus water, may play a key role in the formation of different cluster types.

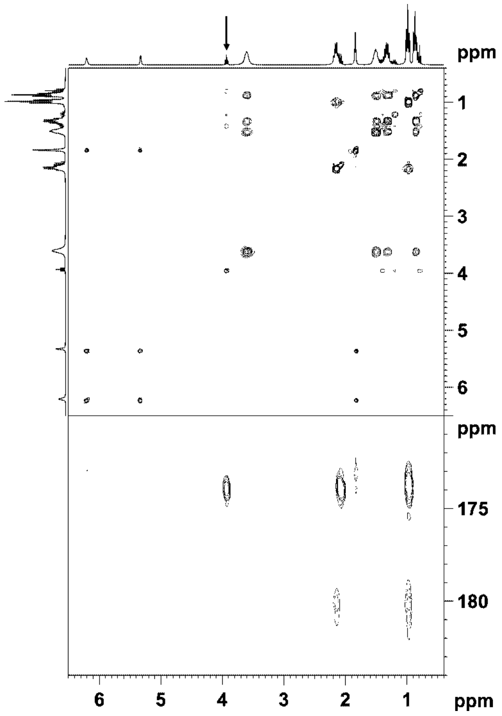

Figure 14. TOCSY spectrum (top) and ^{1}H/^{13}C HMBC spectrum (bottom) of the formation of [Zr$_6$O$_4$(OH)$_4$(propionate)$_3$(methacrylate)$_9$]$_2$ (**6**) after 6 h in [D$_8$]toluene.

Conclusions

The most important conclusion of this work is that **Zr6** and **Zr12** clusters, despite their structural similarity, are not converted into each other in solution under the employed conditions. The first proof is that their solution NMR spectra are clearly different, especially at low temperatures. The spectra are in agreement with the molecular symmetries obtained from the solid-state structures. Second, exchange experiments showed that both Zr$_6$O$_4$(OH)$_4$(propionate)$_{12}$ and [Zr$_6$O$_4$(OH)$_4$(propionate)$_{12}$]$_2$ can be obtained, depending on the preparation route. The **Zr6** cluster Zr$_6$O$_4$(OH)$_4$(propionate)$_{12}$ was obtained by treatment of Zr$_6$O$_4$(OH)$_4$(methacrylate)$_{12}$ (**1**) with a large excess of propionic acid and clearly identified by NMR spectroscopy. On the other hand, the **Zr12** cluster [Zr$_6$O$_4$(OH)$_4$(propionate)$_{12}$]$_2$ was formed either when [Zr$_6$O$_4$(OH)$_4$(propionate)$_3$(methacrylate)$_9$]$_2$ (**6**) was treated with a large excess of propionic acid or directly from Zr(OBu)$_4$ and propionic acid. In either case, the cluster symmetry is retained upon ligand exchange.

From a structural point of view, the **Zr12** clusters are dimers of **Zr6** in which the Zr$_6$ sub-units are connected by four inter-cluster carboxylate bridges. The **Zr12** clusters could be constructed by opening two μ_2- (edge-bridging) carboxylate ligands of **Zr6** and letting two such units dimerize by formation of four inter-cluster bridges. The notion that the **Zr12** clusters could be formed in this manner was imposed by the previous observation that *one* carboxylate ligand opposite the chelated face can be opened to a monodentate coordination and the vacated coordination site occupied by a coordinated alcohol or a water molecule. NMR spectra indicated that this process is reversible.[8] The process leading to the **Zr12** clusters is obviously not related to this. Why *either* **Zr6** *or* **Zr12** clusters are formed when Zr(OR)$_4$ is reacted with carboxylic acids is still an open question. The key to answering this question could be the acidity of the employed carboxylic acids. This influences both the rate of ester plus water formation and also the bond strength of the coordinated carboxylate ligands. The interplay of both probably determines how the cluster formation proceeds in the early stages of the reaction.

Experimental Section

Acetic acid (99%, Aldrich) was dried with CaSO$_4$ and distilled before use. Methacrylic acid (99%, Aldrich) and propionic acid (99.5%, Aldrich) were distilled. Zr(OBu)$_4$ (80% in BuOH, Aldrich), Hf(OBu)$_4$ (95%, ABCR), vinylacetic acid (97%, Aldrich) and dimethylacrylic acid (97%, Aldrich) were used as received. All experiments were carried out in a moisture- and oxygen-free argon atmosphere. To remove the solvate molecules from the crystalline clusters, the compounds were dissolved in CH$_2$Cl$_2$ and all volatiles were removed in vacuo. This process was repeated with toluene and once more with CH$_2$Cl$_2$. The obtained solids were dried at room temperature and ca. 10^{-5} mbar.

All NMR spectra were recorded with a Bruker *Avance* 300 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz) equipped with a 5 mm, inverse-broadband probe head with a *z*-gradient unit. 2D experiments were measured with Bruker standard pulse sequences: COSY (Correlated Spectroscopy), TOCSY (Total Correlation Spectroscopy), HSQC (Heteronuclear Single Quantum Correlation) and HMBC (Heteronuclear Multiple Bond Correlation). Gas-tight Young tubes were used for all measurements. Solvents were either CD$_2$Cl$_2$ (99.8%, euriso-top) or [D$_8$]toluene (99.8%, euriso-top).

Synthesis of $[Zr_6O_4(OH)_4(OOCMe)_{12}]_2\cdot 6MeCOOH\cdot 3.5CH_2Cl_2$ (2): Acetic acid (2.62 g, 43.66 mmol) was added dropwise at room temperature to a solution of $Zr(OBu)_4$ (4.44 mmol, 2.13 g of a 80% solution in BuOH) in CH_2Cl_2 (5 mL) whilst stirring in a Schlenk tube. Within 3 h at room temperature colorless crystals were obtained. The crystals were separated and dried in vacuo. Yield: 864 mg (68%). $C_{63.5}H_{111}Cl_7O_{76}Zr_{12}$ (3433.2): calcd. C 22.22, H 3.26; found C 22.37, H 3.21. IR-ATR: $\tilde{\nu}$ = 2960 (w), 2776 (w), 2607 (w), 1757 (w), 1709 (m), 1599 (s), 1556 (s), 1449 (s), 1346 (m), 1258(m), 1046 (m), 1026 (m), 910 (w), 883 (w), 791 (w), 735 (w), 669 (m) cm^{-1}. ^{1}H NMR (Figure 7) (C_7D_8, 25 °C): δ = 1.82, 1.94, 1.96, 2.01, 2.05 (Me), 10.01 (O*H*). At –40 °C: 1.75, 1.89, 1.90, 1.92, 1.99, 2.02, 2.06 (CH_3), 11.51 ppm (O*H*). ^{13}C NMR (C_7D_8, 25 °C): δ = 181.0, 177.5, 176.6 (*C*O); 23.5, 23.8, 23.7, 22.9, 20.9 (Me). At –40 °C: 181.1, 177.4, 177.3, 177.5, 176.5, 175.9, 175.9 (*C*O); 23.6, 24.1, 23.9, 23.9, 22.8, 23.5, 21.0 ppm (Me).

Synthesis of $[Zr_6O_4(OH)_4(OOCCH_2Me)_{12}]_2\cdot 6MeCH_2COOH$ (3): Propionic acid (1.8 g, 24.2 mmol) was added dropwise at room temperature to a stirred mixture of $Zr(OBu)_4$ (2.37 mmol, 1.14 g of a 80% butanol solution). After 7–8 h at room temperature, colorless crystals (0.53 g) were formed. The crystals were separated and dried in vacuo. Yield 0.53 g (75%). $C_{90}H_{164}O_{76}Zr_{12}$ (3556.9): calcd. C 30.39, H 4.65; found C 29.30, H 4.30. IR-ATR: $\tilde{\nu}$ = 3402 (w), 3259 (w), 2978 (m), 2942 (w), 1717 (m, COOH), 1600 (s, sh, COO), 1533 (s, COO), 1468 (s), 1439 (s, COO), 1374 (m), 1300 (s), 1211 (m), 1078 (m), 1014 (w), 910 (w), 882 (w), 810 (m) cm^{-1}. ^{1}H NMR (Figure 8) (C_7D_8, 25 °C): δ = 1.06, 1.23, 1.35, 1.37, 1.47, 1.49 (Me); 2.20, 2.36, 2.39, 2.55, 2.69, 2.95 (CH_2); 11.96 ppm (O*H*). ^{13}C NMR (C_7D_8, 25 °C): δ = 180.2, 180.8, 179.9, 184.3, 178.6 (*C*O); 28.4, 30.5, 30.5, 30.6, 30.0, 30.2 (*C*H$_2$); 8.5, 9.8, 9.5, 9.5, 9.9, 10.2 ppm (Me).

Synthesis of $[Zr_6O_4(OH)_4(OOCCH_2CH{=}CH_2)_{12}]_2\cdot 6CH_2{=}CH\text{-}CH_2COOH$ (4): Vinylacetic acid (966 mg, 11.22 mmol) was added dropwise to $Zr(OBu)_4$ (1.62 mmol, 776 mg of a 80% solution in BuOH). A microcrystalline precipitate was obtained after 5 min which formed colorless crystals within 2 d at room temperature. The crystals were separated and dried in vacuo. Yield: 332 mg (63%). $C_{120}H_{164}O_{76}Zr_{12}$ (3917.2): calcd. C 36.79, H 4.22, ZrO_2 37.75; found C 36.54, H 4.06, ZrO_2 38.39 (TGA). IR-ATR: $\tilde{\nu}$ = 3396 (w, OH), 3080 (w, CH), 3020 (w, CH), 2982 (w, CH), 1711 (m, C=O), 1641 (w, C=C), 1603 (m, $COO_{as.}$), 1547 (sh, COO_{as}), 1537 (s, COO_{as}), 1436 (s, COO_s), 1417 (s, COO_s), 1392 (s, COO_s), 1314 (w), 1295 (w), 1268 (m), 1199 (m), 1121 (w), 994 (m), 914 (m, C=C), 893 (sh), 811 (m), 782 (sh), 762 (w), 724 (m, CH), 676 (sh), 627 (s, OCO) cm^{-1}. ^{1}H NMR (C_7D_8, 25 °C): δ = 6.43, 6.34, 6.32, 6.30, 5.94 (=C*H*); 5.30/5.14, 5.27/5.11, 5.26/5.17, 5.23/5.09, 5.27/5.12, 5.04/4.96 (CH_2=); 3.61/3.30, 3.57/3.27, 3.33/3.17, 3.29/3.14, 3.28/3.14, 3.00/2.90 (CH_2); 11.55, 7.36, 7.32, 6.88 ppm (O*H*). ^{13}C NMR (C_7D_8, 25 °C): δ = 182.7, 182.5, 182.3, 178.7, 176.9 (*C*O); 135.1, 133.7, 131.0 (=*C*H-); 118.5, 117.1, 115.8 (*C*H$_2$=); 42.1, 41.8, 41.6, 39.5 ppm (*C*H$_2$).

Synthesis of $[Zr_6O_4(OH)_4(OOCCH{=}CMe_2)_{12}]_2\cdot 4Me_2C{=}CHCOOH$ (5): Dimethylacrylic acid (1.23 g, 12.3 mmol) was added to a solution of $Zr(OBu)_4$ (3.25 mmol, 1.56 g of a 80% solution in BuOH) in toluene (5 mL) whilst stirring. The mixture was allowed to stir for an additional 30 min. After 20 days at room temperature colorless crystals separated, which were dried in vacuo. Yield: 0.985 g (88%). $C_{140}H_{208}O_{72}Zr_{12}$ (4137.8): calcd. C 40.64, H 5.07, ZrO_2 35.73; found C 40.58, H 4.87, ZrO_2 35.29 (TGA). IR-ATR: $\tilde{\nu}$ = 3648 (w), 3355 (w, OH), 2911 (w, CH), 1696 (m, C=O), 1651 (s, C=C), 1577 (s), 1520 (br. s, COO_{as}), 1419 (s, COO_s), 1370 (m), 1314 (s), 1234 (m), 1183 (m), 1161 (m), 1077 (m), 862 (m), 819 (m), 722 (m), 638 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 5.57, 5.56, 5.52, 5.57, 5.53, 5.44, 5.37 (C*H*); 2.1, 2.08, 2.07, 1.92, 1.88, 1.79, 1.47 (Me); 10.63 ppm (O*H*). ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 171.5, 174.3, 171.7 (*C*O); 150.7, 152.5, 157.0 (*C*H); 118.3, 120.2, 120.5, 121.7, 121.4, 121.9, 121.1 (*C*Me$_2$), 20.0, 19.9, 20.7, 19.7, 27.0, 27.0, 27.0 ppm (Me).

Synthesis of $[Zr_6O_4(OH)_4(OOCCH_2Me)_3\{OOCC(Me){=}CH_2\}_9]_2\cdot CH_2{=}C(Me)COOH\cdot 5MeCH_2COOH$ (6): Propionic acid (1.37 g, 18.49 mmol) and methacrylic acid (0.618 g, 7.17 mmol) were added dropwise at room temperature to a stirred mixture of $Zr(OBu)_4$ (3.72 mmol, 1.78 g of a 80% butanol solution). After 24 h at room temperature colorless crystals were formed. The crystals were separated and dried in vacuo. Yield: 995 mg (85%). $C_{109}H_{164}O_{76}Zr_{12}$ (3785.1): calcd. C 34.59, H 4.37, ZrO_2 39.06; found C 33.08, H 3.87, ZrO_2 39.49 (TGA). IR-ATR: $\tilde{\nu}$ = 3393 (w, OH), 2979 (m), 1718 (m, COOH), 1595 (s, sh, COO_{as}), 1543 (s, COO_{as}), 1462 (s), 1421 (s, COO_s), 1372 (m), 1302 (s), 1244 (m), 1203 (m), 1080 (m), 936 (m, C=CH$_2$), 826 (m), 617 (m) cm^{-1}. ^{1}H NMR (Figure 10) (C_7D_8, 25 °C): δ = 0.99, 1.11, 1.24, 1.34, 1.40 (CH_3 propionate); 2.11, 2.24, 2.43, 2.57, 2.71 (CH_2 propionate); 6.30, 5.20, 6.40, 5.29, 6.26, 5.25 (CH_2 methacrylate); 11.70 ppm (O*H*). ^{13}C NMR (C_7D_8, 25 °C): δ = 178.3, 179.8, 184.1 (*C*O, methacrylate); 179.8, 179.6, 178.2, 184.2, 183.7 (*C*O, propionate); 137.5, 140.1, 139.9 (*C*Me, methacrylate); 123.1; 123.2; 125.5 (*C*H$_2$, methacrylate); 27.8, 30.2, 30.3, 29.9, 30.2 (*C*H$_2$, propionate); 18.2, 18.5, 18.4 (*C*H$_3$, methacrylate); 8.3, 9.6, 9.3, 9.7, 9.8 (*C*H$_3$, propionate) ppm.

Synthesis of $[Zr_6O_4(OH)_4(OOCMe)_8\{OOCC(Me){=}CH_2\}_4]_2\cdot 6MeCOOH$ (7): Methacrylic acid (239 mg, 2.78 mmol) and acetic acid (423 mg, 7.04 mmol) were added dropwise to $Zr(OBu)_4$ (1.97 mmol, 945 mg of a 80% solution in BuOH) whilst stirring. Colorless needles were formed after 12 h at room temperature. The crystals were washed twice with *n*-heptane (1 mL) and dried in vacuo. Yield: 540 mg (98%). IR-ATR: $\tilde{\nu}$ = 3221 (w, OH), 2980 (vw, CH), 2956 (vw, CH), 2927 (vw, CH), 2875 (vw, CH), 1711 (m, C=O), 1643 (w, C=C), 1595 (sh), 1547 (s, $COO_{as.}$), 1448 (sh), 1422 (s, COO_s), 1373 (m, COO_s), 1344 (w), 1298 (w), 1245 (s), 1207 (sh), 1179 (w), 1047 (w), 1029 (w), 1007 (w), 937 (w), 902 (w), 883 (w), 852 (w), 827 (m), 798 (m), 674 (sh), 644 (vs, OCO), 631 (sh), 612 (vs, OCO) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 6.17/5.66, 6.08/5.59, 6.06/5.59, 5.92/5.39 (CH_2=); 1.82, 1.77, 1.75, 1.68 (Me, methacrylate); 2.00, 1.95, 1.62, 1.47 (Me, acetate); 11.48 ppm (O*H*). ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 189.5, 180.1, 176.4, 175.4, 174.1 (*C*O, acetate); 183.5, 180.1, 171.1 (*C*O, methacrylate); 138.5, 135.9, 135.7, 135.6 (-*C*-); 127.2, 127.1, 126.9, 123.8 (*C*H$_2$=); 22.9, 23.1, 20.5 (Me, acetate); 17.8, 16.6 ppm (Me, methacrylate).

Synthesis of $[Hf_6O_4(OH)_4(OOCMe)_{12}]_2\cdot 6MeCOOH\cdot 3CH_2Cl_2$ (8): Acetic acid (1.92 g, 32.0 mmol) was added dropwise at room temperature to a stirred solution of $Hf(OBu)_4$ (3.2 mmol, 1.57 g of a 95% solution in BuOH) in CH_2Cl_2 (3 mL). After 24 h at room temperature colorless crystals were formed. The crystals were separated and dried in vacuo. Yield: 1.15 g (98%). $C_{63}H_{110}Cl_6Hf_{12}O_{76}$ (4438.1): calcd. C 17.05, H 2.50; found C 17.00, H 2.29. IR-ATR: $\tilde{\nu}$ = 3663 (w), 3387 (w), 1710 (m), 1558 (s), 1453 (s), 1261 (m), 1029 (m), 804 (m), 652 (s), 615 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 1.84, 1.94, 2.01, 2.04, 2.05 (Me), 10.32 (O*H*) ppm. ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 181.9, 177.8, 176.7 (*C*O); 23.5, 23.8, 23.0, 21.8, 21.1 (Me) ppm.

Reaction of $[Zr_6O_4(OH)_4(OOCCH_2Me)_3\{OOCC(Me){=}CH_2\}_9]_2$ (6) with Propionic Acid: An excess (1.94 g, 26.2 mmol) of propionic acid was added to a solution of **6** (165 mg, 0.043 mmol) in benzene (5 mL). The solution was stirred for 10 min, and then all volatile compounds were removed in vacuo. This process was repeated twice.

Reaction of $Zr_6O_4(OH)_4(OMc)_{12}$ (1) with Propionic Acid: An excess (ca. 20 mmol) of propionic acid was added to a solution of **1** (226 mg, 0.133 mmol) in toluene (15 mL). The solution was stirred for 10 min, and then all volatile compounds were removed in vacuo. This process was repeated twice.

X-ray Structure Analyses of 2–8: Data collection (Table 1): The crystals were mounted on a Siemens SMART diffractometer (area detector) and measured in a nitrogen stream. Mo-K_α radiation (λ = 71.069 pm, graphite monochromator) was used for all measurements. The data collection covered a hemisphere of the reciprocal space, by a combination of three or four sets of exposures. Each set had a different φ angle for the crystal, and each exposure took 15 or 20 s and covered 0.3° in ω. The crystal-to-detector distance was 5 cm. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS[12]) was employed. The cell dimensions were refined with all unique reflections. The structures were solved by the direct or the Patterson method (SHELXS97[13]). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL97) with aniso-

Table 1. Crystallographic and structural parameters of **2**–**8**.

	2	**3**	**4**	**5**
Empirical formula	$C_{48}H_{80}O_{64}Zr_{12}\cdot C_{12}H_{24}O_{12}\cdot C_{3.5}H_7Cl_7$	$C_{72}H_{128}O_{64}Zr_{12}\cdot C_{18}H_{36}O_{12}$	$C_{96}H_{128}O_{64}Zr_{12}\cdot C_{24}H_{36}O_{12}$	$C_{120}H_{176}O_{64}Zr_1\cdot C_{20}H_{32}O_8$
Formula weight	3425.2	3556.9	3911.2	4137.8
Temperature [K]	173	173	173	173
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
Unit cell dimension				
a [pm]	1253.71(6)	1709.2(6)	3427.6(2)	1488.19(8)
b [pm]	2415.0(1)	1935.6(6)	2716.7(1)	1722.83(9)
c [pm]	2050.9(1)	2156.1(7)	2075.5(1)	1935.7(1)
α [°]		86.951(7)		90.366(1)
β [°]	104.900(1)	88.241(8)	125.968(1)	93.499(1)
γ [°]		78.973(7)		112.497(1)
Volume [pm^3]·10^6	6000.5(5)	6990 (4)	15641.3(1)	4574.3(4)
Z	2	2	4	1
Calcd. density [g/cm^3]	1.896	1.686	1.660	1.498
Absorption coeff. μ [mm^{-1}]	1.255	0.951	0.859	0.737
Crystal size [mm]	0.34 × 0.10 × 0.09	0.36 × 0.28 × 0.24	0.37 × 0.26 × 0.25	0.30 × 0.30 × 0.30
2θ range [°]	1.92–28.36	1.46–23.26	2.10–28.32	1.76–25.00
Reflections coll./unique	69801/14888	30393/19224	54899/19363	46107/16023
Data/parameters	14888/766	19224/1605	19363/940	16023/1009
GOF on F^2	1.039	1.028	1.016	1.019
R [$I > 2\sigma(I)$]	0.0574	0.070	0.041	0.041
wR_2	0.1415	0.184	0.101	0.112
Largest diff. peak/hole [e·Å^{-3}]	2.293/–1.077	3.211/–1.466	1.248/–0.869	1.452/–1.001

	6	**7**	**8**
Empirical formula	$C_{90}H_{128}O_{64}Zr_{12}\cdot C_4H_6O_2\cdot C_{15}H_{30}O_2$	$C_{64}H_{96}O_{64}Zr_{12}\cdot C_{12}H_{24}O_{12}$	$C_{48}H_{80}Hf_{12}O_{64}\cdot C_{12}H_{24}O_{12}\cdot C_6H_{12}Cl_{12}$
Formula weight	3791.1	3344.2	4678.8
Temperature [K]	213	173	173
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/m$	$P2_1/c$
Unit cell dimensions			
a [pm]	2274.1(2)	3626.9(3)	1255.93(9)
b [pm]	1491.3(2)	1574.1(2)	2419.5(2)
c [pm]	2314.5(2)	1369.8(1)	2049.7(2)
α [°]			
β [°]	111.519(2)	109.385(2)	104.993(1)
γ [°]			
Volume [pm^3]·10^6	7302(1)	7377(1)	6016.3(8)
Z	2	2	2
Calcd. density [g/cm^3]	1.709	1.497	2.583
Absorption coeff. μ [mm^{-1}]	0.916	0.896	10.672
Crystal size [mm]	0.36 × 0.30 × 0.07	0.18 × 0.16 × 0.12	0.21 × 0.18 × 0.12
2θ range [°]	1.74–26.37	2.38–25.00	2.22–25.00
Reflections coll./unique	43785/14908	20132/12844	38319/10582
Data/parameters	14908/901	12844/772	10582/743
GOF on F^2	1.030	1.038	1.289
R [$I > 2\sigma(I)$]	0.037	0.0676	0.076
wR_2	0.091	0.1803	0.149
Largest diff. peak/hole [e·Å^{-3}]	1.032/–0.554	1.259/–0.731	4.319/–2.227

tropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom.

CCDC-604528 (**2**), -604529 (for **3**), -604530 (for **4**), -604531 (for **5**), -604532 (for **6**), -604533 (for **7**), and -604534 (for **8**) 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.

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