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Mono-, Di-, and Trimetallic Methacrylate-substituted Metal Oxide Clusters Derived from Hafnium Butoxide

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Summary. The methacrylate-substituted clusters $Hf_4O_2(OMc)_{12}$, $Hf_6O_4(OH)_4(OMc)_{12}(BuOH)$, $Ti_4Hf_4O_6(OBu)_4(OMc)_{16}$, and $Ti_2Zr_5HfO_6(OMc)_{20}$ ($OMc =$ methacrylate) were prepared by reacting $Hf(OBu)_4$, or $Hf(OBu)_4/Ti(OBu)_4$ and $Hf(OBu)_4/Zr(OBu)_4/Ti(OBu)_4$ mixtures, respectively, with methacrylic acid. All clusters were characterized by X-ray structure analyses and are basically isostructural, although not in each case isomorphous, with the corresponding oxozirconium clusters. Low-temperature NMR studies revealed that the methacrylate ligands of $Hf_4O_2(OMc)_{12}$ are highly dynamic even at $-80°C$.

Keywords. Clusters; X-ray structure determination; Transition metals; Carboxylate ligands; Dynamic processes.

Introduction

We have recently started to develop a new type of inorganic-organic hybrid polymers. These materials are prepared by co-polymerizing unsaturated organic monomers with transition metal oxide clusters substituted by polymerizable organic ligands [1]. A typical example is the polymerization of 0.5–2 mol% of $Zr_4O_2(OMc)_{12}$ ($OMc =$ methacrylate) with methylmethacrylate, methacrylic acid, or styrene as co-monomers. The obtained hybrid polymers, in which the clusters efficiently crosslink the organic polymer chains, have interesting structural and physical properties [2, 3]. It has been shown that the properties of the hybrid polymers not only depend on the cluster/monomer ratio (*i.e.* the crosslinking density), but also on the kind of incorporated cluster [4]. The origin of the latter phenomenon is still unknown, but may be associated with the geometric arrangement of the polymerizable ligands on the cluster surface. The mass ratio between the organic and inorganic components may

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additionally influence the materials properties. However, this possibility was difficult to test due to the lack of clusters having the same structure but a different mass of the inorganic core.

We have previously prepared a variety of oxo zirconium clusters with different shapes and a different degree of substitution by acrylate or methacrylate ligands, such as $Zr_4O_2(OMc)_{12}$ [2, 5], $Zr_6(OH)_4O_4(OMc)_{12}$ [5], $[Zr_6(OH)_4O_4(\text{acrylate})_{12}]_2$ [6], $Zr_6O_2(OR)_{10}(OMc)_{10}$, and $Zr_6O_2(OR)_6(OMc)_{14}$ [17], as well as several methacrylate-substituted Ti/Zr mixed-metal clusters [8]. Given the chemical and structural similarity of zirconium and hafnium compounds in general, there was a good chance that isostructural Hf clusters can be obtained. Since the atomic mass of Hf is about twice that of Zr, polymers reinforced by oxo hafnium clusters would yield a much higher inorganic residue upon pyrolysis. For example, a hybrid polymer obtained by co-polymerization of methylmethacrylate and 1 mol% of $Zr_4O_2(OMc)_{12}$ contains 4.3 wt% ZrO_2, while a polymer with the same portion of the analogous Hf cluster would contain 7.2 wt% HfO_2.

In this paper we report the preparation and structures of some oxohafnium clusters being isostructural with the corresponding oxozirconium clusters, *viz.* $Hf_4O_2(OMc)_{12}$ (**1**) and $Hf_6O_4(OH)_4(OMc)_{12}(BuOH)$ (**2**), and the mixed-metal clusters $Ti_4Hf_4O_6(OBu)_4(OMc)_{16}$ (**3**) and $Ti_2Zr_5HfO_6(OMc)_{20}$ (**4**).

Results and Discussion

The clusters $Hf_4O_2(OMc)_{12}$ (**1**) and $Hf_6O_4(OH)_4(OMc)_{12}(BuOH)$ (**2**) were formed when a 95% solution of $Hf(OBu)_4$ in *Bu*OH was reacted with 4 or 7.5 equivalents of methacrylic acid, respectively. The clusters crystallize from the reaction solution within 1–2 weeks in high yields. The $Hf(OBu)_4$/methacrylic acid ratio necessary to obtain the two clusters is somewhat surprising, because the more highly substituted cluster **1** (three O*Mc* ligands per Hf atom) is formed when a smaller portion of methacrylic acid is employed. In the case of the analogous oxozirconium clusters, the less substituted and more condensed cluster $Zr_6O_4(OH)_4(OMc)_{12}(PrOH)$ was formed from $Zr(OPr)_4(PrOH)$ with 9 equivalents of methacrylic acid [6], while the formation of $Zr_4O_2(OMc)_{12}(PrOH)$ required a 15-fold excess of the acid [5]. The Hf analogue of the alcohol-free cluster $Zr_6O_4(OH)_4(OMc)_{12}$, which was obtained from $Zr(OPr)_4(PrOH)$ and methacrylic acid in a 1:15 ratio, was not obtained.

This difference demonstrates that even small variations in the reaction conditions can lead to clusters of a different composition and structure (although each cluster is reproducibly obtained when the same reaction conditions are employed). The reason for the different reaction behavior may be (slight) differences in the reactivity of the corresponding Zr and Hf alkoxides. The organically substituted metal oxo clusters are formed by three parallel reactions [9]: (i) substitution of one or more alkoxide ligands by carboxylate groups to give $M(OR)_{x-n}(OOCR')_n$, (ii) reaction of the thus liberated alcohol with the carboxylic acid to give an ester and water (where the metal alkoxide may act as a catalyst), and (iii) hydrolysis of all or part of the remaining alkoxide groups by the water generated during esterification. Since there are two alcohol-producing reactions (i and iii) and two carboxylic acid-consuming reactions (i and ii), a difference in the reactivity or catalytic activity of the alkoxides may change the relative rate constants.

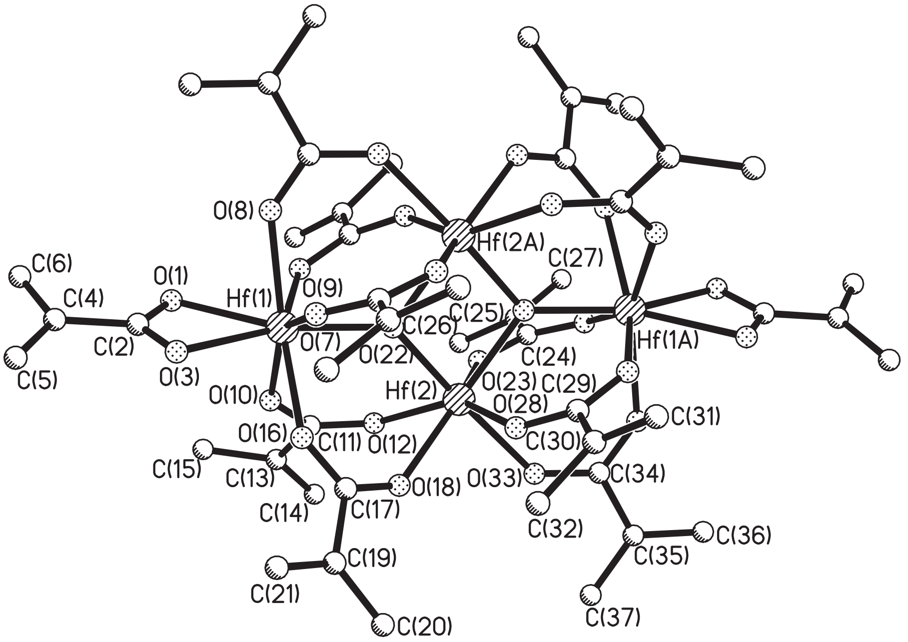

Fig. 1. The molecular structure of $Hf_4O_2(OMc)_{12}$ (**1**); the hydrogen atoms were omitted for clarity; the label "A" refers to symmetry-equivalent atoms (inversion symmetry); Hf(1)–Hf(2) 363.7(3), Hf(1)–Hf(2A) 371.5(3), Hf(1)–Hf(1A) 327.9(3), Hf(1)–O(1) 226.5(5), Hf(1)–O(3) 221.9(5), Hf(1)–O(7) 220.7(5), Hf(1)–O(8) 219.1(5), Hf(1)–O(9) 221.7(5), Hf(1)–O(10) 214.3(5), Hf(1)–O(16) 217.6(5), Hf(1)–O(22) 203.9(4), Hf(2)–O(12) 216.7(5), Hf(2)–O(18) 214.4(5), Hf(2)–O(22) 203.9(5), Hf(2)–O(22A) 209.4(5), Hf(2)–O(23) 214.0(6), Hf(2)–O(28) 215.7(5), Hf(2)–O(33) 214.9(5) pm; Hf(1)–O(22)–Hf(2) 131.3(2), Hf(1)–O(22)–Hf(2A) 123.2(2), Hf(2)–O(22)–Hf(2A) 105.0(2)°

$Hf_4O_2(OMc)_{12}$ (**1**) (Fig. 1) is isostructural – but not isomorphous – with $Zr_4O_2(OMc)_{12}$ [2, 5]. Cluster **1** has crystallographic inversion symmetry, *i.e.* the four hafnium atoms are coplanar. The two Hf_3 sub-units are capped by a μ_3-oxygen atom from different sides. Two of the methacrylate ligands chelate Hf(1) and Hf(1A), respectively, and the other ten bridge the Hf–Hf edges (except the intraannular Hf–Hf). As a result, both central Hf(1) atoms are 7-coordinate (neglecting the Hf–Hf interaction), while the outer Hf(2) atoms are 8-coordinate.

$Hf_4O_2(OMc)_{12}$ (**1**) is highly dynamic in CD_2Cl_2 solution. The room temperature ^1H NMR spectrum (Fig. 2) shows two broad pairs of $=CH_2$ proton signals. The symmetry of the compound in the crystal suggests a maximum of six non-equivalent methacrylate ligands. Although a broadening of the signals was observed at -80°C (Fig. 2), no spectrum corresponding to a static structure was reached. The proton spectra indicate a fast exchange of the O*Mc* ligands at the cluster surface. Such a behavior is not uncommon for carboxylate-substituted clusters [10]. However, the ^{13}C CP/MAS NMR spectrum of $Hf_4O_2(OMc)_{12}$ (Fig. 3) shows nine resolved carboxylate carbons and a broad signal assigned to the $=CH_2$ groups. The larger number of carboxylate carbons, compared to the solid state structure, may be due to polymorphic crystals. For the corresponding cluster $Zr_4O_2(OMc)_{12}$ we found two different crystal structures, with a slightly different coordination of one O*Mc* ligand [2, 5].

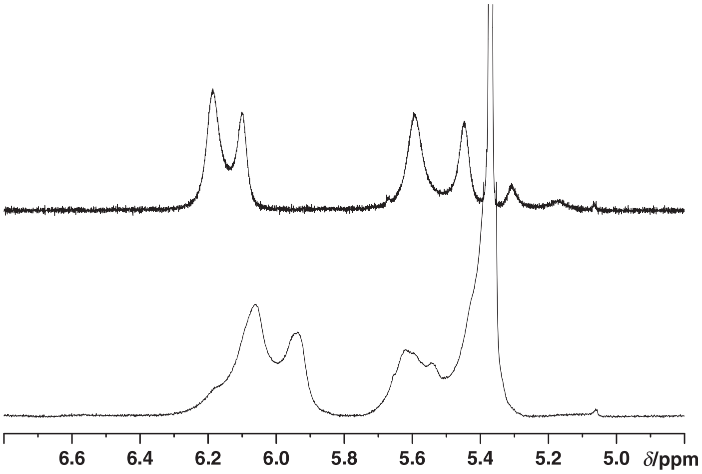

Fig. 2. ^{1}H NMR spectrum of $Hf_4O_2(OMc)_{12}$ (**1**) at room temperature (top) and −80°C (bottom) in CD_2Cl_2 (large signal)

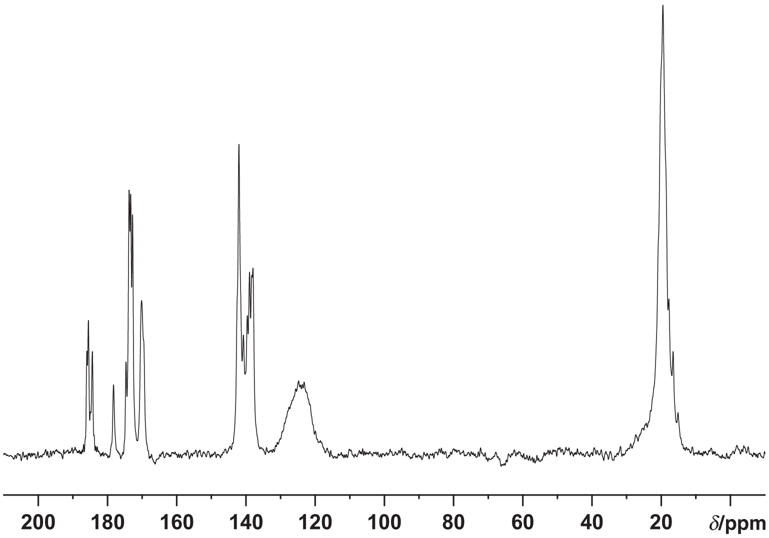

Fig. 3. Solid state ^{13}C CP/MAS NMR spectrum of $Hf_4O_2(OMc)_{12}$ (**1**)

$Hf_6O_4(OH)_4(OMc)_{12}(BuOH)$ (**2**) (Fig. 4) is isostructural to the previously characterized clusters $Zr_6O_4(OH)_4(OOCR)_{12}(PrOH)$ (RCOO = methacrylate or benzoate) [6]. The molecular structure of **2** is derived from the basic structure of $Zr_6O_4(OH)_4(OMc)_{12}$ [5], which consists of a Zr_6 octahedron the triangular faces of which are alternatively capped by μ_3-O or μ_3-OH groups. The O*Mc* ligands bridge the Zr–Zr edges, except one face of the Zr_6 octahedron [corresponding to Hf(1)–Hf(3) in **2**], where the O*Mc* ligands are chelating instead of bridging. The difference between the structures of $Zr_6O_4(OH)_4(OMc)_{12}$ and **2** is that one *bridging* methacrylate ligand is converted in a monodentate ligand, bonded only to Hf(5). The emptied coordination site at Hf(4) is occupied by a coordinated butanol molecule. The long Hf–O distance (Hf(4)–O(69) 225.0(3) pm) clearly excludes the

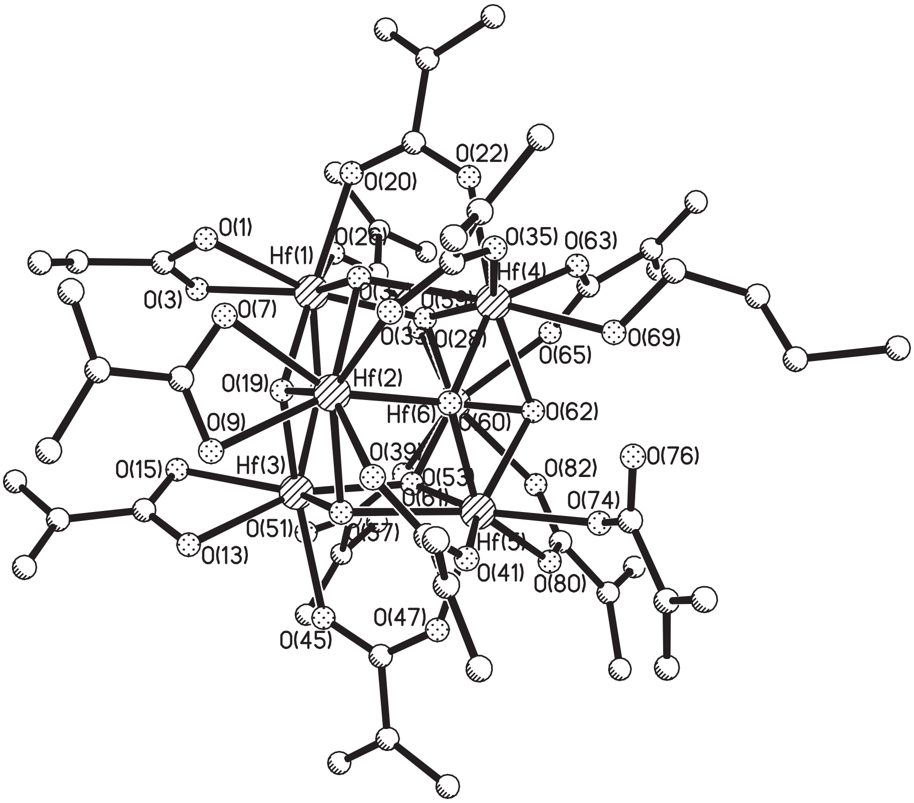

Fig. 4. The molecular structure of $Hf_6O_4(OH)_4(OMc)_{12}(BuOH)$ (**2**); the hydrogen atoms and the hydrogen-bonded methacrylic acid molecules are not drawn for clarity; Hf(1)–Hf(2) 350.70(4), Hf(1)–Hf(3) 348.76(4), Hf(1)–Hf(4) 346.30(4), Hf(1)–Hf(6) 347.94(5), Hf(2)–Hf(3) 351.10(4), Hf(2)–Hf(4) 344.10(4), Hf(2)–Hf(5) 347.51(5), Hf(3)–Hf(5) 346.68(4), Hf(3)–Hf(6) 348.85(5), Hf(4)–Hf(5) 354.52(4), Hf(4)–Hf(6) 347.55(4), Hf(5)–Hf(6) 349.42(5), O(94)···O(62) 277.1(9), O(96)···O(74) 271.7(9), O(90)···O(57) 275.0(9), O(88)···O(13) 270.6(9), O(100)···O(32) 276.1(9), O(102)···O(1) 271.8(9), O(106)···O(15) 272.9(9), O(108)···O(58) 274.5(9) pm

presence of a butoxide ligand instead of a butanol ligand. The carboxylate bridge is opened opposite the chelated face of the Hf_6 octahedron. The spread of Hf–O distances for the μ_3-oxygens [O(19), O(59), O(60), O(61)] is rather small [202.5(3)–210.0(3) pm]. The opening of the methacrylate bridge between Hf(4)/Hf(5) shifts *all* OH bridges closer to a μ_2-bonded situation (two short distances (217.6(4)–225.3(3) pm) and one longer distance (231.2(3)–242.1(3) pm)). The four edges not bridged by methacrylate groups are now in principle bridged by OH groups. All comparable distances (Hf–Hf and Hf–O) in **1** and **2** are slightly shorter than in the analogous Zr clusters.

The crystal structure of **2** (Fig. 5) contains four methacrylic acid molecules per cluster unit, which are hydrogen-bonded to the cluster (the crystal structure of the Zr derivative contains only three methacrylic acid molecules per cluster, and hence the packing of the clusters is different). Each of the μ_3-OH groups of the cluster (O(62), O(57), O(32), O(58)) forms a hydrogen bond with the C=O group of a different methacrylic acid. The OH groups of the methacrylic acid molecules are additionally hydrogen-bonded to oxygen atoms of O*Mc* ligands: two to the oxygen

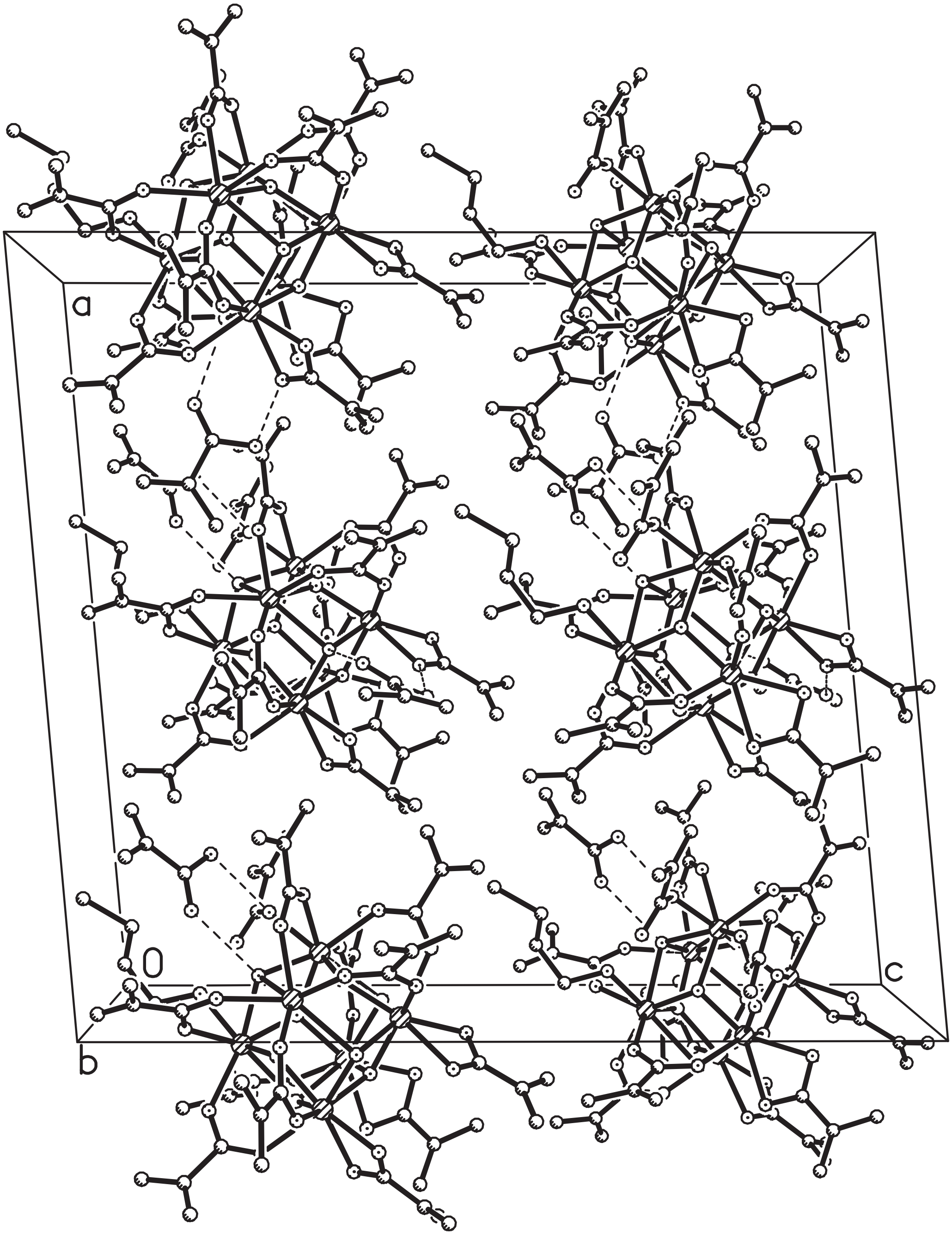

Fig. 5. Packing of **2** (drawn along 010) showing some of the hydrogen bond interactions (dashed lines) between the clusters and the methacrylic acid molecules

atoms of chelating O*Mc* at Hf(3), one to an oxygen atom of chelating O*Mc* at Hf(1) and the fourth to the bonded oxygen atom of the η^1-coordinated O*Mc* at Hf(5). Extensive hydrogen bonding of clusters with μ-OH ligands has also been observed for other metal oxo clusters [5, 6].

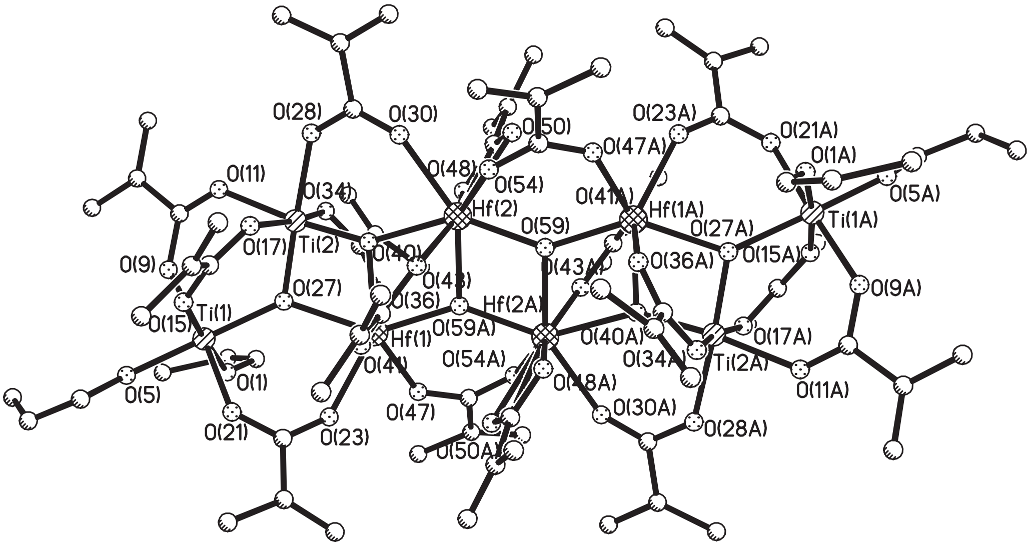

Fig. 6. Molecular structure of $Ti_4Hf_4O_6(OBu)_4(OMc)_{16}$ (**3**); the hydrogen atoms were omitted for clarity; Hf(1)–Hf(2) 346.05(9), Hf(1)–Hf(2A) 386.0(1), Hf(1)–Ti(1) 387.7(3), Hf(1)–Ti(2) 307.5(2), Hf(2)–Hf(2A) 341.7(1), Ti(1)–Ti(2) 341.2(3), Hf(1)–O(27) 217.4(8), Ti(1)–O(27) 200.7(9), Ti(2)–O(27) 185.5(5), Hf(1)–O(59) 205.7(7), Hf(2)–O(59) 204.0(7), Hf(2A)–O(59) 216.0(7) pm; Hf(1)–O(27)–Ti(1) 136.0(4), Hf(1)–O(27)–Ti(2) 99.2(4), Ti(1)–O(27)–Ti(2) 124.1(4), Hf(1)–O(59)–Hf(2) 110.2(3), Hf(1)–O(59)–Hf(2A) 140.8(4), Hf(2)–O(59)–Hf(2A) 108.8(3)°

We have previously obtained a series of four mixed-metal Ti/Zr oxo cluster by reacting $Ti(OBu)_4$ and $Zr(OBu)_4$ with methacrylic acid in different molar ratios. The molecular structures of these clusters were remarkable, as they were based on a common structural theme, *viz.* a zigzag chain of two terminal $[TiO_6]$ octahedra, and two or four central $[ZrO_8]$ or $[ZrO_7]$ polyhedra sharing common edges. The chains are terminated by additional $[TiO_6]$ octahedra or $[ZrO_8]$ dodecahedra [8].

The mixed-metal cluster $Ti_4Hf_4O_6(OBu)_4(OMc)_{16}$ (**3**) (Figs. 6 and 7a) was analogously obtained in 66% yield when $Ti(OBu)_4$, $Hf(OBu)_4$, and methacrylic acid were reacted in a 1:1:9 molar ratio. The reaction conditions were the same as for preparation of the corresponding zirconium cluster $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ to which cluster **3** is isostructural *and* isomorphous [8]. The formation of cluster **3** is taken as a strong indication that the other structural types, observed in the reaction of zirconium and titanium alkoxides [8], could also be obtained for hafnium. However, other $Ti(OBu)_4/Hf(OBu)_4$/methacrylic acid ratios were not investigated.

The isostructural replacement of zirconium by hafnium allowed also the formation of trimetallic oxo clusters containing all three elements of the group IV transition metals. When a 1:1:1 mixture of $Ti(OBu)_4$, $Zr(OBu)_4$, and $Hf(OBu)_4$ was reacted with 12.5 molar equivalents of methacrylic acid, a cluster was obtained that is isostructural with the previously obtained cluster $Ti_2Zr_6O_6(OMc)_{20}$. Refinement of the X-ray structure analysis of **4** (Figs. 7b and 8) showed that four of the Zr positions (Zr(2), Zr(3) and the symmetry-equivalent atoms) are occupied by both Zr(75%) and Hf(25%). Thus, the overall composition of **4** is $Ti_2Zr_5HfO_6(OMc)_{20}$.

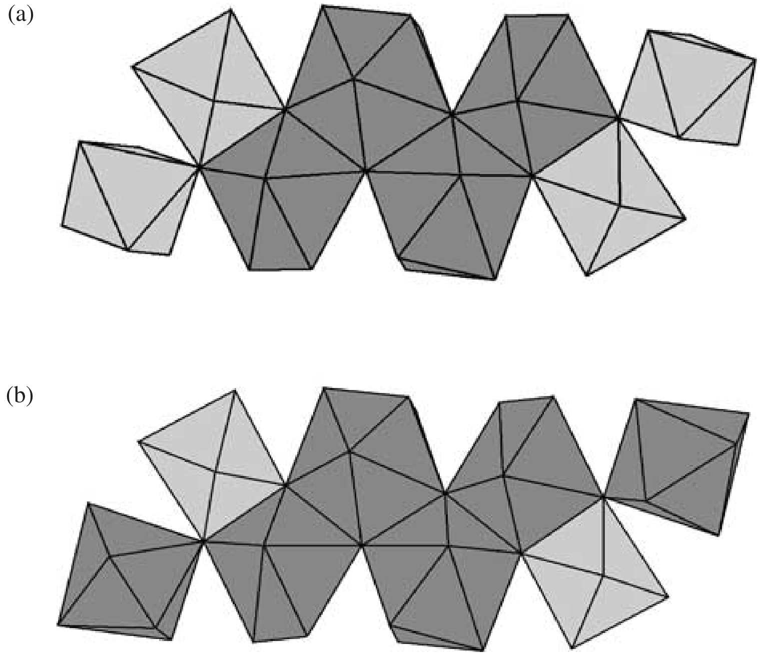

Fig. 7. Core of connected polyhedra of the clusters **3** and **4**: (a) $Ti_4Hf_4O_6(OBu)_4(OMc)_{16}$ (**3**), (b) $Ti_2Zr_5HfO_6(OMc)_{20}$ (**4**); the carbon atoms were omitted in this representation, *i.e.* the corners of the polyhedra represent the oxygen atoms (from any ligand); the light gray octahedra represent the $[TiO_6]$ units

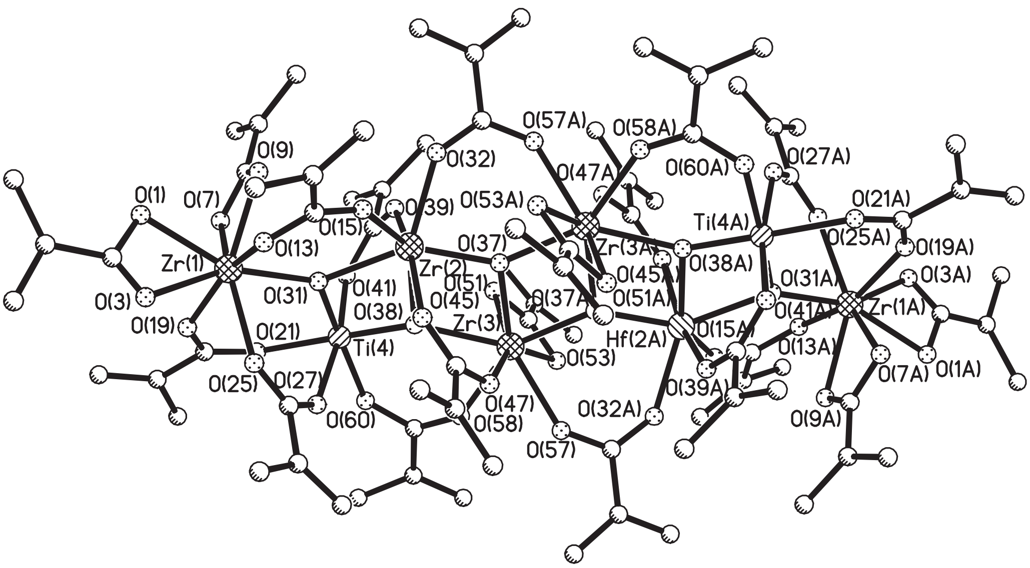

Fig. 8. Molecular structure of $Ti_2Zr_5HfO_6(OMc)_{20}$ (**4**); the hydrogen atoms were omitted for clarity; the atomic positions labelled Zr(2) and Zr(3) have a 75% occupancy of Zr and 25% Hf; Zr(1)–Ti(4) 347.6(2), Zr(1)–Zr(2) 391.9(9), Zr(2)–Zr(3) 346.0(8), Zr(2)–Ti(4) 307.9(1), Zr(3)–Zr(3A) 341.36(9), Zr(3)–Ti(4) 383.3(3), Zr(1)–O(31) 207.2(5), Ti(4)–O(31) 185.1(5), Zr(2)–O(31) 216.8(5), Zr(2)–O(38) 214.2(5), Zr(3)–O(38) 219.8(5), Ti(4)–O(38) 176.4(5) pm; Zr(1)–O(31)–Ti(4) 124.7(2), Zr(1)–O(31)–Zr(2) 135.2(3), Ti(4)–O(31)–Zr(2) 99.7(2), Zr(2)–O(38)–Zr(3) 105.8(2), Zr(2)–O(38)–Ti(4) 103.6(2), Zr(3)–O(38)–Ti(4) 150.5(3)°

The structural motif common to both octanuclear clusters **3** and **4** is a hexanuclear zigzag chain of two [ZrO_8] dodecahedra, two [ZrO_7] pentagonal bipyramids, and two [TiO_6] octahedra sharing edges (Fig. 7). The [TiO_6] octahedra terminate the main chain, while the [ZrO_8] dodecahedra are located in the center of the chain. Two additional polyhedra are condensed to this hexanuclear chain, *viz.* a [TiO_6] octahedron in **3** and a [ZrO_8] dodecahedron in **4**. Details of this structure type have been discussed elsewhere [8].

Conclusions

We have shown in this article, that the methacrylate-substituted oxohafnium clusters can be prepared which are isostructural to the corresponding oxozirconium clusters. This includes mixed-metal clusters with the other group IV transition metals. In inorganic-organic hybrid materials prepared from organofunctional metal oxo clusters, the mass portion of the inorganic residue can thus be easily modified without changing other parameters, especially the structure, composition, or molar ratio of the inorganic building block.

Despite the structural similarities, which are not unexpected bearing in mind that Hf and Zr have essentially the same atomic radii, there are subtle differences. First, the reactivity of $Hf(OBu)_4$ and $Zr(OBu)_4$ appears to be slightly different, as different metal alkoxide/carboxylic acid ratios are needed to get a particular cluster type. Second, when $Zr(OBu)_4$ is reacted, the highly condensed, prototypical cluster $Zr_6O_4(OH)_4(OMc)_{12}$ is obtained in a wide range of conditions. This cluster type was not obtained for Hf, only cluster **2** in which the cluster core is the same, but the ligand arrangement is somewhat different.

Experimental

All operations were carried out in *Schlenk* tubes under an Ar atmosphere. The alkoxides and methacrylic acid were used as received.

Preparation of $Hf_4O_2(OMc)_{12}$ (**1**)

An amount of 0.58 g of methacrylic acid (6.74 mmol) was added dropwise under stirring to 0.836 g of 95% $Hf(OBu)_4$ (1.68 mmol) in *n*-butanol. Stirring at room temperature was continued for 1 h, and then the mixture was allowed to stand at 4°C for 15 d, resulting in the separation of colorless crystals of **1**. The mother liquid was decanted from the crystals, and the crystals were dried at moderate vacuum to yield 0.54 g (73%) of **1**.

Preparation of $Hf_6O_4(OH)_4(OMc)_{12}(BuOH)$ (**2**)

An amount of 0.722 g of methacrylic acid (8.38 mmol) was added dropwise to a stirred solution of 0.522 g of 95% $Hf(O^nBu)_4$ (1.11 mmol) in *n*-butanol in 2 cm^3 of benzene. Stirring at room temperature was continued for 1 h, and then the mixture was allowed to stand at 4°C for 20 d, resulting in the separation of colorless crystals of **2**. The mother liquid was decanted from the crystals, and the crystals were dried at moderate vacuum to yield 0.25 g (51%) of **2**.

Preparation of $Ti_4Hf_4O_6(OBu)_4(OMc)_{16}$ (**3**)

An amount of 1.26 g of methacrylic acid (14.7 mmol) was added dropwise under stirring to a mixture of 0.815 g of 95% $Hf(OBu)_4$ (1.64 mmol) in *n*-butanol and 0.630 g of $Ti(OBu)_4$ (1.85 mmol). Stirring at room temperature was continued for 1 h, and then the mixture was allowed to stand at 4°C for 15 d, resulting in the separation of colorless crystals of **3**. The mother liquid was decanted from the crystals, and the crystals were dried at moderate vacuum to yield 0.72 g (66%) of **3**. $C_{80}H_{98}Hf_4O_{42}Ti_4$ (2637.1) Found: C 35.9; H 3.7; Calc.: C 36.2; H 4.3.

Preparation of $Ti_2Zr_5HfO_6(OMc)_{20}$ (**4**)

An amount of 1.94 g of methacrylic acid (22.5 mmol) was added dropwise under stirring to a mixture of 0.90 g of 80% $Zr(OBu)_4$ (1.9 mmol) in *n*-butanol, 0.9 g of 95% $Hf(OBu)_4$ (1.8 mmol) in *n*-butanol, and 0.66 g of $Ti(OBu)_4$ (1.9 mmol). The solution was stirred at room temperature for 1 h and was then allowed to stand at 4°C for 20 d, resulting in the separation of colorless crystals of **4**. The mother liquid was decanted from the crystals, and the crystals were dried at moderate vacuum to yield 1.53 g (30%) of **4**.

NMR Spectroscopy

One and two dimensional spectra in solution were recorded on a Bruker Avance 300 at 300.13 MHz (^1H) and 75.47 (^{13}C). Solid state spectra (^{13}C CP/MAS) were recorded on a Bruker Avance 300, standard bore magnet equipped with a 4 mm probe at 299.97 MHz (^1H) and 75.41 (^{13}C). The rotor speed was 10 kHz.

X-Ray Structure Analyses of **1–4**

Data collection (Table 1): The crystals were mounted on a Siemens SMART diffractometer (area detector) and measured in a N_2 stream. Mo-K_α radiation ($\lambda = 71.069$ pm, graphite monochromator)

Table 1. Crystallographic and structural parameters of **1–4**

	1	**2** · 4 HO*Mc*	**3**	**4**
Empirical formula	$C_{48}H_{60}Hf_4O_{26}$	$C_{68}H_{93}Hf_6O_{41}$	$C_{80}H_{98}Hf_4O_{42}Ti_4$	$C_{80}H_{80}HfO_{46}Ti_2Zr_5$
Formula weight	1767.0	2637.4	2637.1	2507.8
Space group	$P2_1/n$	Cc	$C2/c$	P-1
a/pm	1332.7(14)	2321.0(3)	2762.4(7)	1331.8(2)
b/pm	1691.0(11)	1545.1(2)	1581.2(4)	1332.1(2)
c/pm	1367.9(14)	2487.0(3)	2672.4(7)	1663.1(2)
α/deg				97.089(3)
β/deg	95.12(5)	95.159(2)	117.789(4)	92.489(3)
γ/deg				104.734(3)
V/pm^3	$3070(5) \cdot 10^6$	$8883(2) \cdot 10^6$	$10327(4) \cdot 10^6$	$2823(1) \cdot 10^6$
Z/Calcd. density/ g · cm^{-3}	2/1.911	4/1.972	4/1.734	1/1.475
μ/mm^{-1}	6.816	7.068	4.473	1.571
Crystal size/mm	0.7 × 0.5 × 0.36	0.46 × 0.40 × 0.34	0.80 × 0.36 × 0.16	0.36 × 0.30 × 0.24
θ range/deg	2.41–28.36	1.75–30.02	1.67–26.37	1.59–26.37
Reflections coll./ unique	20053/7588	33093/22136	28626/10451	17296/11449
Data/parameters	7588/353	22136/1041	10451/569	11449/613
GOF	1.119	0.988	1.108	1.049
$R1$ ($I > 2\sigma(I)$)	0.046	0.024	0.066	0.058
$wR2$	0.117	0.051	0.147	0.156
Largest diff. peak and hole/e · Å^{-3}	4.005/–3.798	1.392/–0.809	4.386/–1.922	1.224/–1.026

was used for all measurements. The cell dimensions were refined with all unique reflections. The data collection (**1**: 183 K, **2** and **4**: 213 K, **3**: 193 K) covered a hemisphere of the reciprocal space, by a combination of three sets of exposures. Each set had a different ϕ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The crystal-to-detector distance was 4.40 cm. The reflections were corrected for polarization and *Lorentz* effects, and an empirical absorption correction (SADABS) was employed.

The structure was solved by direct methods (SHELXS86). The positions of the hydrogen atoms were calculated according to an idealized geometry. Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL93) with anisotropic thermal parameters for all non-hydrogen atoms. The parameters of the hydrogen atoms were refined with a riding model. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge C82 1EZ, UK (fax int. code +(1223) 336-033, e-mail: teched@ccdc.cam.ac.uk) quoting the depository numbers CCDC 202866 (**1**), 202867 (**2**), 202868 (**3**), or 202869 (**4**).

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