

Review

Clusters with a Zr_6O_8 core

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ABSTRACT

Clusters with the resilient $Zr_6O_4(OH)_4$ core are important building blocks for metal-organic framework structures and cluster-reinforced polymers. The triangular faces of a Zr_6 octahedron are capped by μ_3 -O and/or μ_3 -OH groups, and the Zr_6 cluster core is surrounded by a shell of organic ligands, mostly carboxylate ligands. The basic chemistry of $Zr_6O_4(OH)_4(OOCR)_{12}$ clusters and their dimers is reviewed, including modifications of the ligand shell and expansion of the cluster core by means of additional zirconium atoms or other transition metals.

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1. Introduction

Clusters with a Zr_6O_8 core (or, more precisely, $Zr_6O_{8-x}(OH)_x$) belong to the group of metal oxo clusters with a high symmetry, next to clusters with a trigonal M_3O or tetrahedral M_4O core. The Zr_6O_8 core consists of a Zr_6 octahedron the triangular faces of which are capped by μ_3 -O and/or μ_3 -OH groups. The high symmetry makes the Zr_6 clusters, along with other properties, attractive as building blocks for inorganic-organic hybrid materials (see Section 6).

The Zr_6O_8 core is the smallest possible structural section of tetragonal zirconia, where each zirconium atom is surrounded by eight oxygen atoms, and each oxygen atom by four zirconium atoms (μ_4 -O). The Zr_6O_8 cluster core is dissected from the ZrO_2 structure by converting the μ_4 -O into μ_3 -O or μ_3 -OH, retaining the bonds between the oxygen atoms and the zirconium atoms of an (octahedral) Zr_6 subunit. The thus obtained Zr_6O_8 unit is stabilized by (mostly) organic ligands, which also allow the Zr atoms to become 8-coordinate again (as in ZrO_2).

The prototypical carboxylate-substituted clusters $Zr_6O_4(OH)_4(OOCR)_{12}$ and derivatives thereof are synthesized by

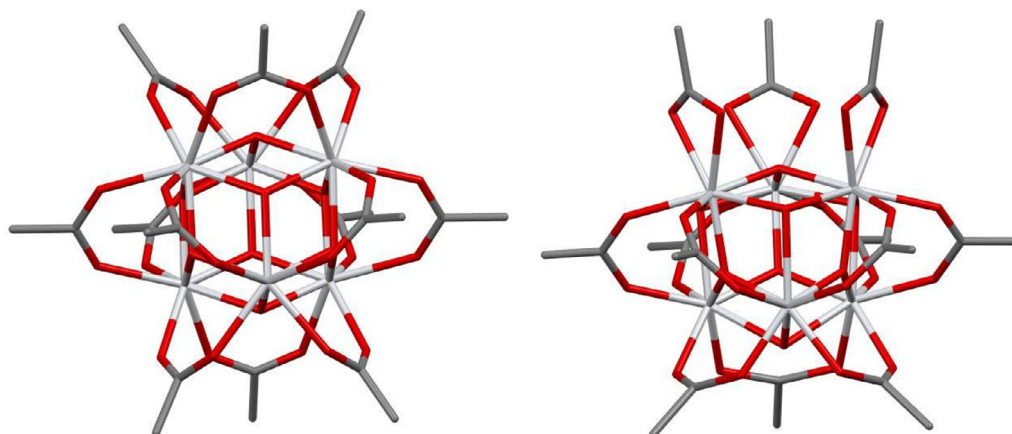


Fig. 1. The two structure types of $Zr_6O_4(OH)_4(OOCR)_{12}$. Left: O_h -symmetry; right: C_{3v} -symmetry. The substituents of the RCOO ligands were omitted for clarity.

adding a sub-stoichiometric amount of water to a hydrolysable molecular precursor in the presence of carboxylic acids or carboxylate anions. In addition to zirconium alkoxides, $Zr(OR)_4$, “inorganic precursors” are also used, such as ZrX_4 ($X = Cl$, acetylacetonate), $ZrOX_2$ ($X = Cl$, NO_3) or $Zr(OH)_2CO_3$. There are two general synthesis protocols: (i) Slow (intended or accidental) water addition to the precursor solution (exposure to ambient moisture, hydrated metal salts as precursors, etc.) and (ii) for $Zr(OR)_4$ precursors, *in situ* generation of water by ester formation. In the latter case, the carboxylic acid serves two purposes: to provide carboxylate ligands for capping the cluster core and to react with the alcohol, which is eliminated upon substitution of OR against carboxylate groups. Other cluster types may also be obtained [1], depending on the reaction conditions.

In this article, the basic chemistry of molecular Zr_6O_8 clusters with monocarboxylate ligands will be outlined, providing a basis for the use of such clusters as building blocks in extended metal-organic network structures.

2. $Zr_6O_4(OH)_4(OOCR)_{12}$ structures: bridging vs chelating carboxylate ligands

In the clusters $Zr_6O_4(OH)_4(OOCR)_{12}$, the triangular faces of the Zr_6 octahedron are alternatively capped by μ_3-O and μ_3-OH groups. Each zirconium atom is coordinated by eight oxygen atoms (two μ_3-O , two μ_3-OH and four oxygen atoms of carboxylate ligands) with square antiprismatic geometry. From simple structural considerations one expects that the twelve carboxylate ligands bridge the twelve edges of the Zr_6 octahedron. Such an octahedral geometry (O_h , if the difference between μ_3-O and μ_3-OH is neglected) is not only found in many metal-organic network structures (MOF) with Zr_6 clusters as the connectors (see Section 6.2), but also in some $Zr_6O_4(OH)_4(OOCR)_{12}$ derivatives with monocarboxylate ligands, such as $R = Me$ [2], *t*Bu or CMe_2Et [3] (Fig. 1, left). The clusters are isostructural with $U_6O_4(OH)_4[O_2P(OPh)_2]_{12}$, with bridging diphenylphosphate instead of carboxylate ligands [4].

In contrast, the X-ray structure analyses of $Zr_6O_4(OH)_4(OOCR)_{12}$ with RCOO = methacrylate [5] or *endo* 5-norbornene-2-carboxylate [6] show that part of the carboxylate ligands is differently coordinated (Fig. 1, right). Three carboxylate ligands chelate the zirconium atoms at one μ_3-O capped face (“chelated face”), while the other nine RCOO groups bridge all edges of the Zr_6 octahedron except the ones of the chelated face. The cluster core thus is C_{3v} symmetric with the C_3 axis passing through the center of the chelated face and the triangular face opposite to it, and the mirror planes bisecting these faces. In the room temperature 1H and ^{13}C

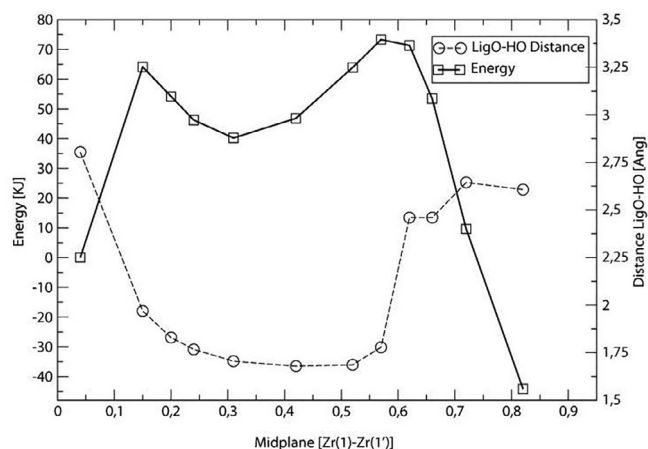
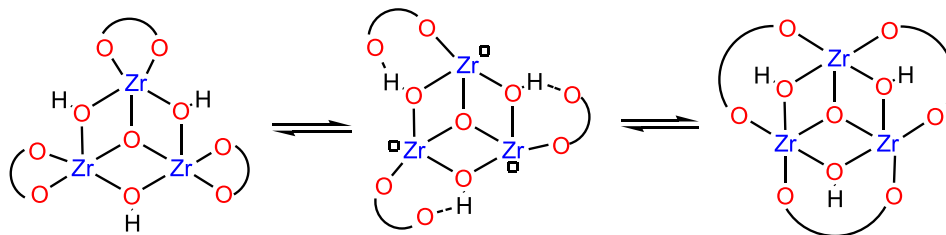


Fig. 2. Left scale: Energy profile for the ligands movement from chelating to bridging. Zero at the reaction coordinate corresponds to the original chelated Zr and 1 for the neighboring Zr'. Right scale: distance between the moving carboxylate oxygen and the hydrogen of the μ_3-OH group (from Ref. 8).

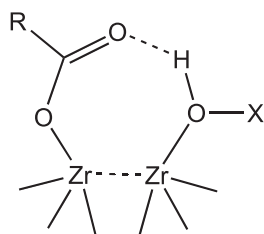
NMR spectra of $Zr_6O_4(OH)_4(OOC-CMe=CH_2)_{12}$, the signals can be clearly assigned to three non-equivalent ligand positions (one chelating and two different bridging positions) according to the C_{3v} symmetry of the cluster in the crystalline state [7].

The C_{3v} structures in the solid state and in solution are somewhat surprising. As a matter of fact, DFT calculations for $Zr_6O_4(OH)_4(OOCH)_{12}$ showed that an O_h -symmetric cluster is lower in energy by 44.13 kJ than the C_3 -symmetric cluster [8]. The most likely explanation is that the latter clusters undergo extensive hydrogen bonds to co-crystallizing carboxylic acids by which the C_3 structure is stabilized (the clusters act both as hydrogen donors [OH groups] and hydrogen acceptors). The same may be true in solution, where the presence of additional carboxylic acids, solvent effects or inter-cluster hydrogen bonds cannot be excluded.

The pathway for the conversion of chelating into bridging carboxylate ligands (or vice versa) was investigated by molecular dynamics calculations for $Zr_6O_4(OH)_4(OOCH)_{12}$ [8]. Starting with the C_{3v} structure it was assumed that all chelating ligands rearrange simultaneously from chelating to bridging as one oxygen atom of each chelating ligand moves to a neighboring Zr in a synchronized fashion. Bonding of one oxygen of the chelating formate was retained and the other oxygen atom was allowed to move freely perpendicular to the reaction coordinate. It strikes that there is a minimum in the energy surface for this movement between the



Scheme 1. Concerted movement of the carboxylate ligands at the “chelated face” (\circ = carboxylate ligand; \square = vacant coordination site).



Scheme 2. Bonding of ROH (X = R) or H₂O (X = H) in the adducts.

chelating and bridging configuration (*i.e.*, between the start and the end of the movement) (Fig. 2). This minimum corresponds to the shortest distance between the moving oxygen and the hydrogen of the μ_3 -OH group and is thus due to an intermediate hydrogen bonding interaction with a μ_3 -OH group, as indicated in Scheme 1.

Alcohol adducts of the composition $Zr_6O_4(OH)_4(OOCR)_{12}(R'OH)$, namely $Zr_6O_4(OH)_4(OOCR)_{12}(PrOH)$ (R = Ph, CMe=CH₂) [9], $Zr_6O_4(OH)_4(exo-5-norbornene-2-carboxylate)_{12}(BuOH)$ [6] and $Zr_6O_4(OH)_4(OOC-CMe=CH_2)_8(OOC-CHMe_2)_4(BuOH)$ [7], and analogously the water adduct $Zr_6O_4(OH)_4(OOC-CHMe_2)_{12}(H_2O)$ [7], are a slight variation of the “C_{3v} structure”. To enable coordination of the alcohol or water molecule, one carboxylate ligand opposite the “chelated face” is only monodentate rather than edge-bridging. The alcohol or water molecule is coordinated to the thus opened coordination site at the neighboring Zr atom and undergoes a hydrogen bond with the oxygen atom of the monodentate carboxylate ligand (Scheme 2). Apart from this modification, the structure of the clusters is retained. The adducts $Zr_6O_4(OH)_4(OOCR)_{12}(XOH)$ indicate that the triangular face of the Zr₆ octahedron opposite the “chelated face” appears to be somewhat activated.

The carboxylate-XOH combination shown in Scheme 2 can be regarded as an enlarged bidentate ligand forming a 7-membered metallacycle. In the derivatives $[Zr_6O_4(OH)_4(OOC-CH_2NMe_3)_{12}(H_2O)_4]^{12+}$ [10] and $Zr_6O_4(OH)_4(OOC-CHPh_2)_{12}(MeOH)_4$ [11], four such “enlarged ligands” were found. While eight carboxylate ligands bridge an axial and an equatorial Zr atom of the Zr₆ octahedron, the other four remaining ligands are “enlarged” through hydrogen-bonding with coordinated water or alcohol molecules as shown in Scheme 2 and bridge the four equatorial Zr atoms.

Such findings show that hydrogen-bond interactions play an important role in the (structural) chemistry of Zr₆ clusters. A side note: hydrogen atoms often cannot be located, especially in the presence of heavy atoms. The most obvious evidence for hydrogen bond interactions, in the cases discussed here, are O...O distances of around 250–270 pm. Allocation of the hydrogen atom to a certain oxygen atom is not always obvious and therefore different forms of chemical formulae can be found in the literature. For the sake of consistency, carboxylate ligands are always considered deprotonated in this article and, correspondingly, OH/OR protonated (*i.e.*, H₂O or ROH ligands).

A variation of the “chelated face” motif was observed in centrosymmetric $Zr_6O_6(OH)_2(OOC-CH_2Ph)_{10}(phen)_2$ (phen = 1,10-phenanthroline) [12], where two (opposite) Zr₃ faces are differ-

ent from the others. One Zr atom of these faces is chelated by a carboxylate ligand, the second by a (chelating) phen ligand and the third by a monodentate carboxylate with a hydrogen bond to the adjacent μ_3 -OH. The latter renders the corresponding Zr atom only 7-coordinate. Owing to the replacement of two negatively charged carboxylate by two neutral phen ligands, two μ_3 -OH groups are converted into μ_3 -O for charge balancing reasons.

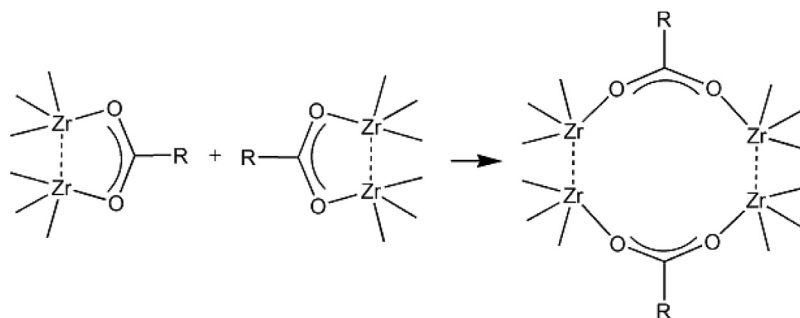
A special case is $Zr_6O_4(OH)_4(OOC-N_2H_3)_{12}$, where all carboxylate ligands are chelating (2 per Zr atom). However, coordination of the ligands is through only one oxygen atom of the COO groups and the terminal nitrogen atom of the hydrazine moieties, resulting in 5-membered metallacycles [13]. This cluster is isostructural with $Ce_6O_4(OH)_4(acac)_{12}$ [14].

3. Dimers and oligomers of $Zr_6O_4(OH)_4(OOCR)_{12}$

The adducts $Zr_6O_4(OH)_4(OOCR)_{12}(XOH)$ show that bridging carboxylate ligands can be opened, leaving a vacated coordination site at one Zr atom which is then occupied by a XOH molecule. In a similar manner, bridging carboxylate ligands of two Zr₆ units can be pairwise opened and converted in bridges connecting two Zr₆ units (“inter-Zr₆ bridges”) as schematically shown in Scheme 3. Instead of interacting with a coordinated XOH molecule, the de-coordinated oxygen atoms of the “opened” carboxylate ligands are then bonded to the vacated coordination site of a second Zr₆ unit. The bridging of two cluster units by a monocarboxylate ligand, *i.e.*, coordination of the two COO oxygen atoms to different metal atoms, is an important difference to MOFs, where di-, tri- or tetrapotic carboxylate ligands are the linkers, *i.e.*, where both oxygen atoms of each COO group are bonded to the same metal atom.

Converting one carboxylate ligand per Zr₆ unit into an inter-Zr₆ bridge would result in a (Zr₆)₂ dimer in which the two Zr₆ units are connected via two carboxylate bridges. No structure of this type is known. If two carboxylate bridge per Zr₆ unit are opened, either chains of interconnected Zr₆ units, [Zr₆]_∞, or dimers [Zr₆]₂ could be formed, depending on the relative position of the opened carboxylate ligands within the Zr₆ unit, but only the dimers were experimentally obtained until present,

In the dimers $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ (Fig. 3), two carboxylate bridges per Zr₆ unit opposite the “chelated face” of the C_{3v}-type structure are opened. This results in [Zr₆]₂ structures with a total of four inter-Zr₆ carboxylate bridges. Several dimers of this type were isolated and structurally characterized, with R = Me [15], Et [15,16], CH₂CH₂SH [17], CH₂CH=CH₂ [15], (CH₂)₃C≡CH [18], CH=CH₂ [9] and CH=CMe₂ [15] as well as mixed-ligand clusters with both methacrylate and acetate or butyrate ligands [15]. In each case, additional hydrogen-bonded carboxylic acid molecules co-crystallize, as in many Zr₆ clusters. Although the Zr₁₂ clusters are formally Zr₆ dimers, the two cluster types are not interconverted under the conditions employed during their synthesis [15]. Depending on the reaction conditions either Zr₆ or Zr₁₂ clusters are formed reproducibly. They can be clearly distinguished in solution by their NMR spectra.



Scheme 3. Conversion of intra-cluster into inter-cluster bridging carboxylate ligands.

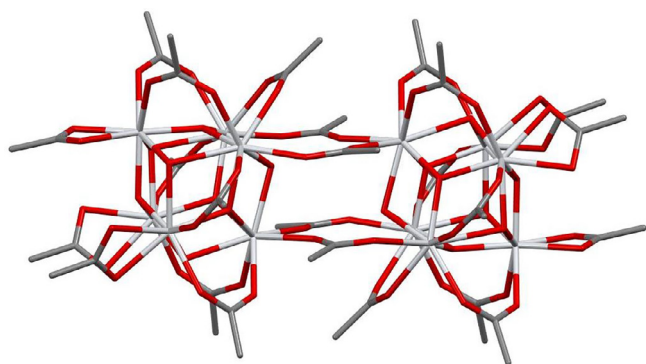


Fig. 3. The general structure of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OOCR})_{12}]_2$. The substituents of the RCOO ligands were omitted for clarity.

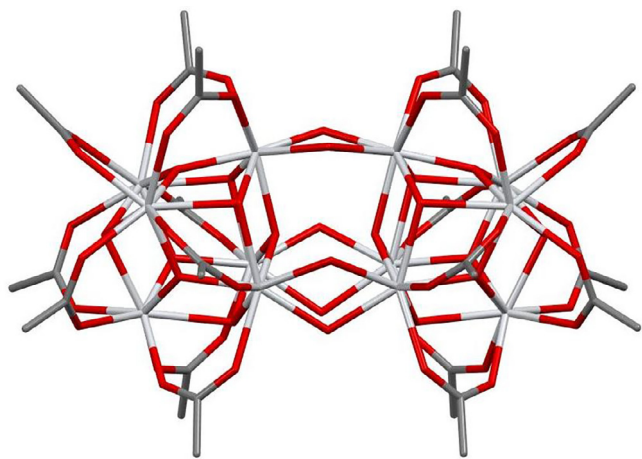


Fig. 4. The structure of $[\text{Zr}_6\text{O}_4(\text{OH})_7(\text{OOC-CH}_2\text{tBu})_9]_2$ [19]. The tBu substituents were omitted for clarity.

In the $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OOCR})_{12}]_2$ structures, one carboxylate ligand opposite the “chelated face” remains bridging. From a structural point of view, conversion of the remaining bridging ligands (one in each Zr_6 unit) into additional inter- Zr_6 carboxylate bridges should be possible, *i.e.*, the resulting $(\text{Zr}_6)_2$ structures would have six inter-cluster bridges. Such structures have not been observed until present. However, a derivative has been isolated, *viz.* $[\text{Zr}_6\text{O}_4(\text{OH})_7(\text{OOC-CH}_2\text{tBu})_9]_2$ [19], where six μ_2 -OH groups bridge the Zr_6 units (Fig. 4). All carboxylate ligands are intra- Zr_6 bridges (no chelating carboxylates).

The same $\text{Zr}_{12}\text{O}_{22}$ core was observed in $[\text{Zr}_{12}\text{Co}_2\text{O}_8(\text{OH})_{14}(\text{OOCtEt})_{22}(\text{MeCN})_2(\text{pyrazine})]_{\infty}$, where two Co complex moieties are linked to the outer sphere of the $\text{Zr}_{12}\text{O}_{22}$ unit (and opposite

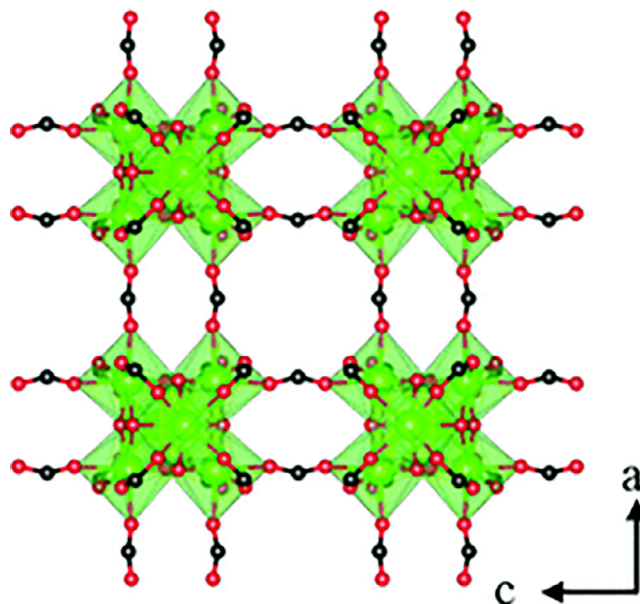


Fig. 5. A layer of interconnected Zr_6 polyhedra in $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OOCH})_{12}]_{\infty}$ (from Ref. 22).

the μ_2 -O bridges) only via bridging carboxylate ligands (without a Zr–O–Co linkage). Pyrazine units bridge the Co atoms, thus resulting in a polymeric structure [20].

The two possibilities to connect two Zr_6 units with each other, *viz.* carboxylate bridges or μ_2 -O, are also found in the compounds $\text{Zr}_{36}\text{O}_{24}(\text{OH})_{52}(\text{OOCH})_{44}$ and $\text{Zr}_{36}\text{O}_{24}(\text{OH})_{48}(\text{OOCH})_{48}$, consisting of rings of six Zr_6 units ($=[\text{Zr}_6]_6$) [21]. In one $[\text{Zr}_6]_6$ derivative the Zr_6 octahedra are interconnected by four sets of 6 μ -OH and two sets of 2 μ -OH + 2 formate groups. In the other derivative, three sets of 6 μ -OH groups alternate with three sets of mixed μ -OH/formate linkers. This is equivalent to an average of *three* opened carboxylate bridges per Zr_6 unit. The cyclic compounds can also be regarded as a dimer of $[\text{Zr}_6]_3$ units or as a trimer of $[\text{Zr}_6]_2$ units, respectively.

In another formate derivative, $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OOCH})_{12}]_{\infty}$, the four bridging ligands in the equatorial plane of the O_h -type $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OOR})_{12}$ structure are converted into inter- Zr_6 ligands [22]. This results in a two-dimensional, layered structure as shown in Fig. 5. The carboxylate ligands connecting the apical and equatorial Zr atoms remain bridging.

4. Modified ligand sphere

The ligand sphere of the Zr_6O_8 cluster core can be varied to some extent. In most cases, the ligands are supplied during the

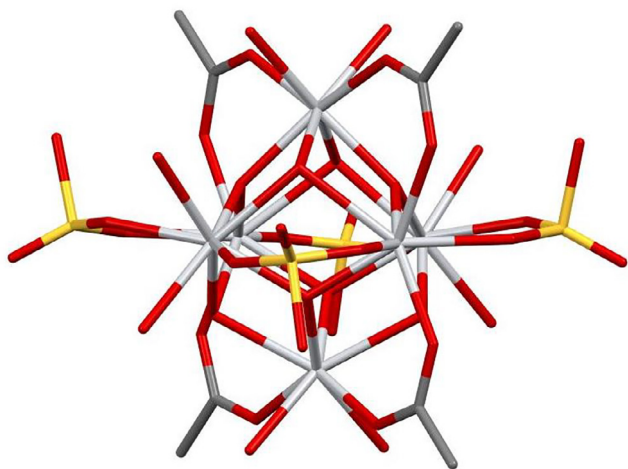


Fig. 6. The structure of $Zr_6O_4(OH)_4(OOCMe)_4(SO_4)_4(H_2O)_8$ [25]. Yellow: sulfur atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cluster synthesis. However, post-synthetic ligand exchange is also possible. Following the observation that the methacrylate ligands of $Zr_6O_4(OH)_4(\text{methacrylate})_{12}$ undergo degenerate exchange with methacrylic acid in solution, addition of an excess of propionic or isobutyric acid to a solution of the cluster allowed complete exchange of the methacrylate ligands [7,15]. Partial exchange was also possible. For example, the mixed-carboxylate cluster $Zr_6O_4(OH)_4(\text{methacrylate})_8(\text{isobutyrate})_4(\text{BuOH})$ was isolated [7]. Similar results were obtained for $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ clusters [15]. An associative mechanism for carboxylate exchange was postulated, where the key intermediate is similar to Scheme 2, viz. coordination of a carboxylic acid ($X = C(O)R$) hydrogen-bonded to a η^1 -coordinated carboxylate ligand [7].

Ligand exchange with preservation of the cluster core is only unproblematic, if the entering and leaving ligand have the same charge and similar coordination characteristics [23]. Along this line, reaction of $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ ($R = \text{Et}, \text{CH}_2\text{CH} = \text{CH}_2$) with acetylacetone led to the selective substitution of one chelating carboxylate ligand per Zr_6 unit and formation of isostructural $[Zr_6O_4(OH)_4(OOCR)_{11}(\text{acac})]_2$; no substitution of bridging carboxylate ligands was observed [24].

Clusters with different anionic ligands can also be obtained by employing acid mixtures for cluster syntheses. For example, the aforementioned $Zr_6O_4(OH)_4(\text{methacrylate})_8(\text{isobutyrate})_4(\text{BuOH})$ was also prepared from $Zr(\text{O}Bu)_4$ and a mixture of propionic and isobutyric acid [7] and the clusters $Zr_6O_4(OH)_4(OOCR)_4(SO_4)_4(H_2O)_8$ (Fig. 6, $R = \text{H}, \text{Me}, \text{Et}$) from $ZrOCl_2$ and a mixture of RCOOH and sulfuric acid [25]. Since sulfate is a dianionic ligand, four carboxylate and four sulfate ligands (instead of 12 carboxylate ligands) are sufficient for compensating the charge of the $Zr_6O_4(OH)_4$ cluster core. The SO_4 ligands bridge the four metal atoms in the equatorial plane of the Zr_6 octahedron and the four carboxylate ligands every second edge between an axial and equatorial Zr atom. Since the carboxylate ligands are arranged in one plane, both axial and two equatorial Zr atoms are only surrounded by six oxygen atoms of the O, OH, sulfate and/or carboxylate groups. The typical eight-coordination of the Zr atoms in Zr_6O_8 clusters is reached by coordinating two water molecules to the under-coordinated Zr atoms.

In $[Zr_6O_4(OH)_4(OOCR)_8(H_2O)_8]^{4+}$ ($R = \text{CH}_2\text{NH}_3^+$ [26,27], Ph [28]) and $Zr_6(\mu_3\text{-OH})_8(\text{bis}(3,5\text{-dimethylpyrazol-1-yl)acetate})_8(\text{OH})_8$ [29], the carboxylate ligands bridge *all* apical-equatorial edges of the Zr_6 octahedron. In the former clusters, each equatorial Zr atom

is coordinated by two water molecules, and in the pyrazolylacetate derivative by two OH groups. For charge compensation reasons, all $\mu_3\text{-O}$ in the latter compound are protonated (note, however, the previous remark on the difficult assignment of proton positions).

If external water is provided to the reaction mixture, metal salts rather than acids can also be the source of the ligands capping the Zr_6O_8 core. $[Zr_6O_4(OH)_4(OOCMe)_5(\text{AsW}_9\text{O}_{33})_2(\text{H}_2\text{O})_2]^{11-}$ was thus obtained by adding $ZrCl_4$ to an aqueous solution of $\text{Na}_9[\text{AsW}_9\text{O}_{33}]$ and lithium acetate [30]. Each $\text{AsW}_9\text{O}_{33}^{9-}$ “ligand” is capping a Zr_3 triangle of the $Zr_6O_4(OH)_4$ unit with six $Zr\text{-O-W}$ bonds (two per Zr atom). The two capped triangles face each other at the bottom half of the Zr_6 octahedron. From a structural point of view, the two $\text{AsW}_9\text{O}_{33}^{9-}$ moieties thus replace six bridging carboxylate groups.

5. Modification of the cluster core

Several clusters were isolated where the Zr_6O_8 core is expanded either by additional Zr or other metal atoms. The additional atoms are either bonded to the Zr_6 unit via the capping $\mu_3\text{-O/OH}$ groups or by means of new $\mu\text{-O}$. They are additionally connected to the Zr_6 unit via bridging organic ligands, which easily adapt to modified metal oxide cluster cores [23].

The cluster cores of $Zr_{10}O_8(\text{O}Bu)_{16}(\text{OOC-C}_6\text{H}_4\text{CH}_2\text{Cl})_8$ [31] and $Zr_{10}O_4(OH)_4(\text{OPr})_{20}(\text{O}_3\text{PPh})_4$ [32] are expansions towards a bigger section of the tetragonal zirconia structure. They can be regarded as condensation products between $Zr(\text{O}Bu)_4$ and the $\mu_3\text{-OH}$ groups of $Zr_6O_4(OH)_4$ units, with concomitant rearrangement of the organic ligands. The $Zr_3(\mu_3\text{-OH})$ groups are thus converted into $Zr_4(\mu_4\text{-O})$ units (as in ZrO_2), but otherwise the Zr_6O_8 core is preserved (Fig. 7, left). A Zr_4 super-tetrahedron is formed in which the Zr_6 octahedron is inscribed.

In the previous examples, the Zr_6 core is expanded by binding additional Zr atoms to its $\mu_3\text{-OH}$ groups. Another possibility is condensation of the Zr_6O_8 unit with other Zr units by means of new $\mu\text{-O}$. In the salicylate derivative $Zr_{10}O_6(OH)_4(\text{OOC-C}_6\text{H}_4\text{O})_8(\text{OOC-C}_6\text{H}_4\text{OH})_8$, two Zr_2 units are added to two *trans*-Zr atoms of the $Zr_6O_4(OH)_4$ core via $\mu_3\text{-O}$ groups (Fig. 7, center) [33]. The structure of $Zr_{26}O_{18}(OH)_{30}(\text{OOCH})_{38}$ [34] can be broken down in five interconnected Zr_6O_8 subunits (Fig. 7, right) in which the four equatorial Zr atoms of the central unit are also part of the outer Zr_6 octahedra.

Expansion of the $Zr_6O_4(OH)_4$ core is also possible with other metals, resulting in heterometallic clusters. The $\mu_3\text{-OH}$ groups are relatively acidic (see above) and therefore the hydrogen atoms can be replaced by metal ions. When $Zr_6O_4(OH)_4(\text{OOC-CHMe}_2)_{12}$ was reacted with a mixture of $[\text{Fe}_3\text{O}(\text{OOC-CHMe}_2)_6]\text{NO}_3$, Ln (NO_3)₃ (Ln = La, Ce, Pr, Nd) and *N*-butyl- or *N*-methyl-diethanolamine (H_2L), heterometallic clusters $Zr_6\text{Fe}_2\text{Ln}_2\text{O}_8(\text{OOC-CHMe}_2)_{14}\text{L}_2(\text{NO}_3)_2$ were obtained in which the two Fe and two Ln complex moieties are coordinated to the former $\mu_3\text{-OH}$ groups. The cluster core is thus the same as that of the $Zr_{10}O_8$ clusters (Fig. 7, left), with Fe and Ln instead of the outer Zr atoms [35].

The $Zr_7\text{Pb}_3\text{O}_8$ core of the cluster $Zr_7\text{Pb}_3\text{O}_8(\text{O}i\text{Pr})_{10}(\text{OOCMe})_8$ [36] has the same basic structure as that of the $Zr_{10}O_8$ and $Zr_6\text{M}_4\text{O}_8$ clusters. However, one of the Zr atoms of the central Zr_6 octahedron is replaced by a Pb atom. $\text{Zr}(\text{O}^i\text{Pr})_2$ groups are condensed to the two $\mu_3\text{-OH}$ groups to which the core Pb atom is bonded, while the other two $Zr_3\text{-OH}$ groups are converted into $Zr_3\text{-O-Pb}$ groups. The $Zr_3\text{-O-Zr}$ and $Zr_3\text{-O-Pb}$ groups are additionally supported by bridging ligands.

Other derivatives have been isolated in which only two or three $Zr_3\text{-OH}$ groups of the basic $Zr_6O_4(OH)_4$ unit are converted into $Zr_3\text{-O-M}$ groups ($M = \text{Fe}, \text{Mn}$ or Ni) [37].

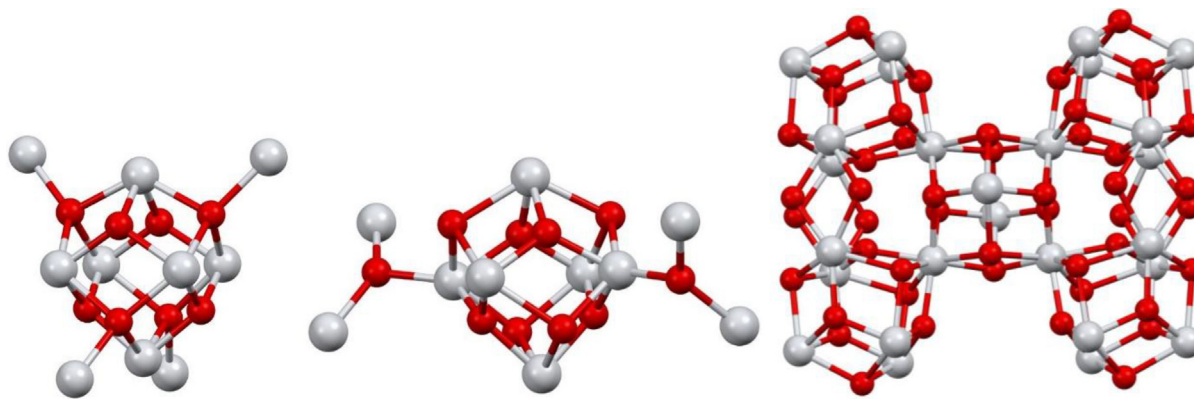


Fig. 7. The expanded cluster cores of $Zr_{10}O_8(OR')_{16}(OOCR)_8$ and $Zr_{10}O_4(OH)_4(OR')_{20}(O_3PR)_4$ (left), $Zr_{10}O_6(OH)_4(OOC-C_6H_4O)_8(OOC-C_6H_4OH)_8$ (center) and $Zr_{26}O_{18}(OH)_{30}(OOCH)_{38}$ (right).

There are also examples in which additional metal complex moieties are not only bonded to the former μ_3 -OH groups of the Zr_6 octahedron, but also to the μ_3 -O. In $[Zr_6M_6O_8(OOCR)_{12}(HL)_6]^{2+}$ ($H_2L = N$ -butyldiethanolamine; $M = Ni$, $R = CHMe_2$ [37]; $M = Co$, $R = Et$ [20]), six ML groups are bonded to the Zr_6O_8 core via the four μ_3 -OH and two μ_3 -O sites. The “vacant” μ_3 -O are trans to each other, the six M atoms thus span a strongly distorted octahedron in which the regular Zr_6 octahedron is inscribed.

The basic building blocks of $[Zr_{12}M_3O_{11}(OH)_{11}(OOEt)_{20}(HL)(H_2L)_2(bpy)]_2$ ($M = Co, Ni$; $H_2L = N$ -methyldiethanolamine, $bpy = 4,4'$ -bipyridine) [38] are two $Zr_{12}O_{22}$ units, as in $[Zr_6O_4(OH)_7(OOCR)_9]_2$ (Fig. 4). In each of them, one of the μ_2 -O connecting the two Zr_6 octahedra is converted into a Zr_2-O-M unit. Moreover, two Co or Ni complex moieties are coordinated to the outer sphere of the $Zr_{12}O_{22}$ unit, opposite the μ_2 -O bridges, as in the aforementioned $Zr_{12}Co_2$ cluster [20]. Bipyridine ligands bridge the outer M atoms of the two $Zr_{12}MO_{22}$ units and thus result in a cyclic dimer.

6. Networks of interconnected Zr_6O_8 clusters

The clusters $Zr_6O_4(OH)_4(OOC-CMe=CH_2)_{12}$ and $[Zr_6O_4(OH)_4(OOC-CH=CH_2)_{12}]_2$ are resistant to water at pH 7 and air. In contrast, they are converted into unidentified lower-nuclearity or polymeric structures under acidic or alkaline conditions [39]. $Zr_6O_4(OH)_4(OOC-CMe=CH_2)_{12}$ thermally decomposes in air at ca. 400 °C to give ZrO_2 . Thermolysis in solution at 400 °C in the presence of stabilizing agents resulted in the formation of phase-pure tetragonal zirconia nanoparticles [40]. It was shown that $Zr_6O_4(OH)_4$ units in MOFs can be reversibly dehydroxylated to Zr_6O_6 units [41].

Due to their high thermal and hydrolytic stability, $Zr_6O_4(OH)_4$ clusters are very interesting building blocks for inorganic-organic network structures. The interlinking of the clusters through organic groups can either be done by copolymerization of suitably substituted clusters with organic monomers (to give cluster-reinforced polymers [42–44]) or by di-, tri- or tetra-topic carboxylate ligands (to give Zr_6 -based MOFs [45]). Since good review articles are available in both cases, also addressing the properties of such materials, only a short outline on Zr_6 -based polymers and MOFs will be given in the following, mainly with regard to the issues discussed before.

6.1. Cluster-reinforced polymers

The carboxylate ligands of the clusters must have functional organic groups R to allow for polymerization either neat or with organic co-monomers. Most Zr_6O_8 -based hybrid polymers were

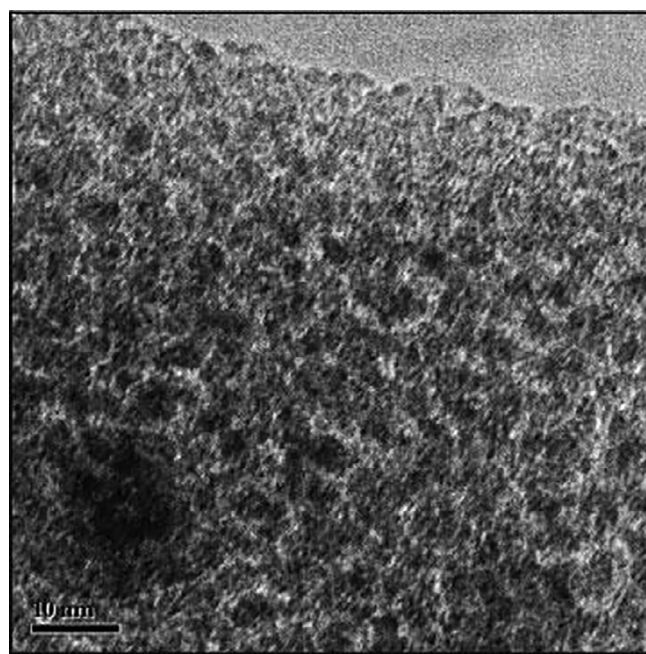


Fig. 8. Bright field TEM of a film obtained from $[Zr_6O_4(OH)_4(OOC-CH_2CH_2SH)_{12}]_2$ and an allylpentaerythritol/trimethylolpropane-tris-(3-mercaptopropionate) mixture (from Ref. 50).

prepared by free-radical (co-)polymerization of unsaturated organic compounds and small amounts of (meth-)acrylate or vinylacetate-substituted $Zr_6(OH)_4O_4(OOCR)_{12}$ or $[Zr_6(OH)_4O_4(OOCR)_{12}]_2$ [46–49]. Other polymerization methods are also possible, if the groups R are appropriate. Thus, Zr_6 clusters with norbornene carboxylate ligands were employed in ring-opening metathesis polymerization [6] or clusters with 4-pentynoate ligands for alkyne-azide click reactions [18]. Thiol-ene reactions were performed either by reacting 3-mercaptopropionate-substituted clusters with olefinic compounds [17,50] or methacrylate-substituted clusters with thiols [51,52].

EXAFS investigations of some polymers showed that the integrity of the Zr_6 clusters is retained upon polymerization [17,53]. Whether all twelve functional ligands per Zr_6 unit are involved in the formation of the polymers, or how many, is difficult to figure out. X-ray diffraction methods cannot be applied for gathering structural information because the cluster-containing polymers are amorphous. Distribution of the clusters in the polymers is a critical issue with regard to the polymer properties. Most of the

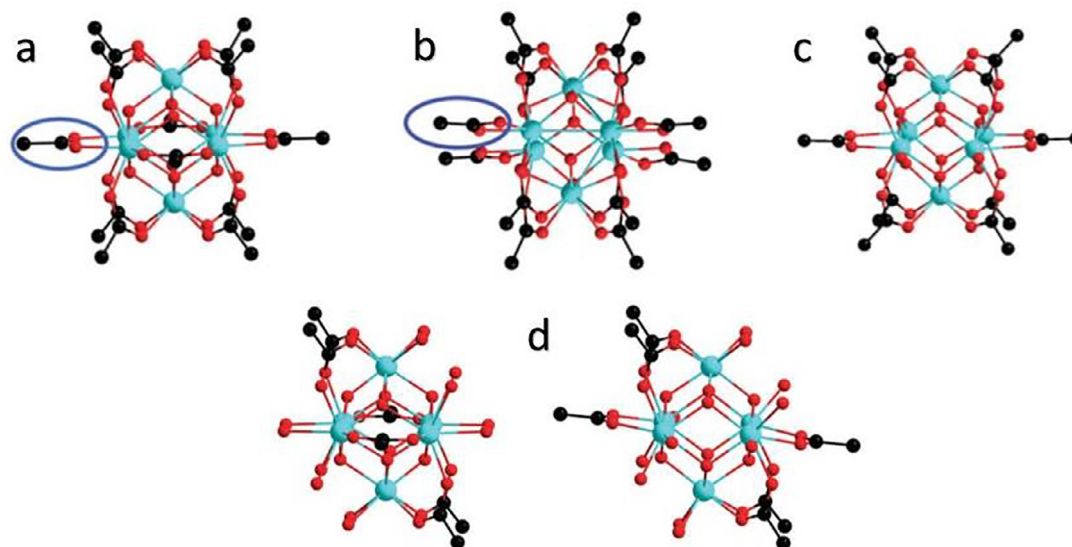


Fig. 9. The substitution pattern of some Zr_6 cluster units in MOFs. Only the COO groups of the polytopic carboxylates are shown. a,b: 12-connected units with only bridging COO groups within the Zr_6 units (a) or 8 bridging and 4 chelating COO groups (b); c: 10-connected DUT-69; d: 6-connected $Zr_6O_4(OH)_4(OOC \sim COO)_3(OH)_6(H_2O)_6$ (adapted from Ref. 45).

hybrid polymers are transparent, indicating a random distribution of the Zr_6 clusters. This was supported by TEM (Fig. 8) and SAXS [47,48,50], although some „clustering of the clusters“ cannot be excluded [42,46,47].

6.2. Metal-organic framework structures

Synthesis protocols for MOFs with Zr_6O_8 clusters as connector units are very similar to that for clusters with monocarboxylate ligands, viz. reaction of Zr precursors with carboxylic acids or ligand exchange starting with pre-formed Zr_6O_8 clusters. The reactions can be promoted by sonochemical, hydrothermal, microwave-assisted, etc. methods.

When Zr precursors are reacted with polytopic carboxylic acids alone, crystallinity, crystal size and morphology of the MOFs are hard to control, and aggregates of nanocrystals are often obtained. This was improved by the so-called modulated synthesis strategy [54], where monocarboxylic acids are used as modulators together with the polytopic carboxylic acids. Experimental evidence was provided for Zr_6 -based MOFs that metal precursor and modulator initially form intermediates, possibly molecular Zr/O clusters, followed by exchange of the monocarboxylate for polytopic ligands [55]. The nucleation rate of the MOFs can thus be controlled by varying the proportion of the modulator.

As a matter of fact, Zr_6 MOFs can be prepared by a deliberate two-step protocol. In a first example, the cluster $Zr_6O_4(OH)_4(-OOC-CMe=CH_2)_{12}$ was reacted with muconic or terephthalic acid, resulting in the same MOFs as in the reaction of $ZrCl_4$ with the dicarboxylic acids [56].

Zr_6 MOFs can be obtained with different numbers of connector ligands per Zr_6O_8 unit (Fig. 9) [45]. The most common topologies are based on 12-connected $Zr_6O_4(OH)_4$ units, that is, COO groups of 12 polytopic linkers are coordinated to each Zr_6 . Arrangement of the carboxylate ligands in Fig. 9a is equivalent to that of the molecular $Zr_6O_4(OH)_4(OOCR)_{12}$ clusters with O_h symmetry, i.e., the 12 COO groups bridge all edges of the Zr_6 octahedron (as in MOF UiO-66 [41]). An alternative for 12-connected $Zr_6O_4(OH)_4$ units, with no equivalent molecular cluster, is that the four COO groups in the equatorial plane of the Zr_6 octahedron are chelating

rather than bridging (Fig. 9b, as in MOF PCN-223 [57]). In 10-connected $Zr_6O_4(OH)_4(2,5\text{-thiophenedicarboxylate})_5(OOCMe)_2(H_2O)_2$ (DUT-69 [58], Fig. 9c), two equatorial edges of the Zr_6 octahedron are blocked by the two acetate ligands (the modulators) and water molecules and thus cannot contribute to network formation. In 8-connected Zr-MOFs (not shown in Fig. 9), the eight carboxylate ligands only bridge the apical-equatorial edges of the Zr_6 octahedron, similar to the aforementioned $Zr_6(O/OH)_8(OOCR)_8$ derivatives, and the Zr atoms of the equatorial plane are coordinated by OH/ H_2O . Two different arrangements of the six COO groups at each Zr_6 octahedron were found for 6-connected MOFs of the composition $Zr_6O_4(OH)_4(OOC \sim COO)_3(OH)_6(H_2O)_6$ (Fig. 9d). Coordination of the Zr_6 unit is completed by OH/ H_2O , as for the 8-coordinated MOFs.

7. Conclusions

Zr_6O_8 is a very resilient structural unit. It can be regarded as the smallest structural section of tetragonal ZrO_2 , consisting of a Zr_6 octahedron capped by eight $\mu_3\text{-O}$ and/or $\mu_3\text{-OH}$ groups. In molecular clusters, the $Zr_6(O/OH)_8$ unit is protected by bridging or chelating bidentate ligands, typically carboxylate ligands. OH ions or water molecules can partly take the place of the bidentate ligands without affecting the Zr_6O_8 core structure, with hydrogen-bond interactions playing a very important role. The variable number of carboxylate ligands around the same cluster core is, *inter alia*, an interesting feature for obtaining Zr_6 -MOFs with different topologies. Preservation of the $Zr_6(O/OH)_8$ unit was also seen in polymerization reactions of appropriately substituted clusters. The octahedral Zr_6 unit can be expanded by additional zirconium or other metal atoms, again evidencing the robustness of this building block.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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