

FROM MOLECULES TO NETWORKS



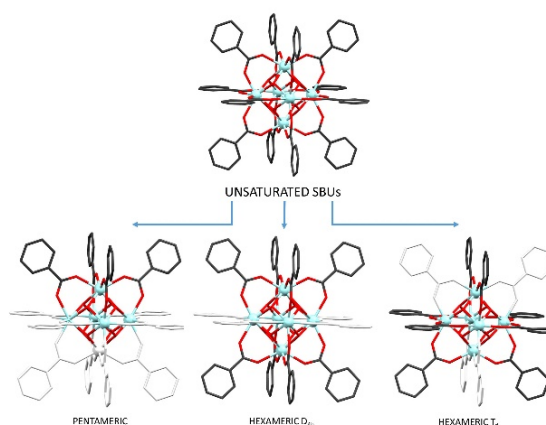
Synthesis and structure of nanomaterials based on zirconium/carboxylate clusters

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Abstract. Zirconium-carboxylate clustering processes in alcohol/water mixtures are analyzed using monocarboxylic benzoic and hydroxybenzoic acids. Mass-spectroscopy data indicates the presence of hexa- and pentanuclear species and the acid-base nature and pH dependence of the transformation between both species. The X-ray diffraction studies of compounds showed that they are closely related to the $[\text{Zr}_6(\text{O})_4(\text{OH})_4(\text{OOCR})_{12}]$ SBU found in many MOFs by removing carboxylic ligands, $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu\text{-OOCR})_8(\text{H}_2\text{O})_8]^{4+}$, or by additionally removing one of the metal centers, $[\text{Zr}_5(\mu_3\text{-O})_2(\mu_3\text{-OH})_6(\mu\text{-OOCR})_4(\text{H}_2\text{O})_{11}(\text{alcohol})]^{6+}$. Hexameric clusters exhibit different dispositions of their eight carboxylato ligands in such a way that the remaining four carboxylate-free positions are arranged according to a square planar or tetrahedral symmetry. The pentameric clusters are unprecedented nuclearity cores and its isolation provides a novel building block for the design of metal-organic materials.



Introduction

Clustering chemistry is a key point in the design of the secondary building units (SBUs) that comprise metal-organic frameworks (MOFs).^{1,2} Until recently, novel topologies of MOF emerged basically from the change of the organic linkers and the other constituent, and the metallic nodes (SBUs) seem to be less explored. This fact is evident in the zirconium/carboxylate MOF family which is mostly based on neutral $[\text{Zr}_6(\text{O})_4(\text{OH})_4(\text{OOCR})_{12}]$ SBU. Therefore, there is great interest in developing novel architectures based on low-cost aromatic polycarboxylic ligands by modifying the features of the SBUs and a deep research on the formation of these polynuclear entities is required.³ Herein, we have thoroughly analyzed the formation of discrete zirconium-oxide-hydroxide entities in alcoholic media using monocarboxylic benzoato and hydroxybenzoato ligands to avoid the polymerization that would hinder this kind of studies. A crucial stage of the setup of the Zr–O/OH polynuclear entities resides on the oxygen source from which these species emerge and a precise control of the amount of water is crucial for the first steps of formation. On the other hand, the acidity of the reaction media exerts a strong influence on the deprotonation of the coordinated water molecules to afford bridging hydroxide and oxide anions but also on the readiness of the carboxylic ligands to coordinate to the metal centers.

We report on discrete zirconium entities ranging from the hexanuclear $[\text{Zr}_6(\text{O})_4(\text{OH})_4(\text{L})_8(\text{H}_2\text{O})_8]^{4+}$ clusters (L = benzoato, 2-hydroxybenzoato, and 3-hydroxybenzoato), obtained by capping some of the linking positions of the $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]^{12+}$ core with the anionic forms of monocarboxylic ligands, to $[\text{Zr}_5(\text{O})_2(\text{OH})_6(\text{L})_4(\text{H}_2\text{O})_{11}(\text{ROH})]^{6+}$ species (L = benzoato; R = Et and Pr) containing an unknown pentameric $[\text{Zr}_5(\mu_3\text{-O})_2(\mu\text{-OH})_2(\mu\text{-OH})_4]^{10+}$ core. The coordination of the carboxylic ligands in the octahedral shaped hexanuclear entities can be frozen in a cationic intermediate state in which only some of the available positions are occupied, leaving these carboxylato unsaturated SBUs (Figure 1).

In solid-state, non-covalent interactions coming from the hydroxyl-substituted positions direct the arrangement of the monocarboxylic ligands towards different symmetries regarding the unoccupied carboxylato positions: these have been placed in a square arrangement for benzoato and 3-hydroxybenzoato ligands and in a tetrahedral one for the 2-hydroxybenzoato ligand.

Synthesis of Compounds

$[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu\text{-OOC}\text{C}_6\text{H}_5)_8(\text{H}_2\text{O})_8]\text{Cl}_4 \cdot \text{EtOH} \cdot 35\text{H}_2\text{O}$ (**1**), $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu\text{-OOC}\text{C}_6\text{H}_5)_8(\text{H}_2\text{O})_8]\text{Cl}_4 \cdot 15\text{H}_2\text{O}$ (**2**), and $[\text{Zr}_5(\mu_3\text{-O})_2(\mu_3\text{-OH})_6(\mu\text{-OOC}\text{C}_6\text{H}_5)_4(\text{H}_2\text{O})_{11}(\text{EtOH})]\text{Cl}_6 \cdot 2\text{EtOH} \cdot 10\text{H}_2\text{O}$ (**5**). 0.3870 g of ZrCl_4 dissolved in 4.8/0.2 mL of an ethanol/water solution was added dropwise to an 8 mL ethanol solution containing 0.4054 g of benzoic acid. The resulting colorless solution was basified

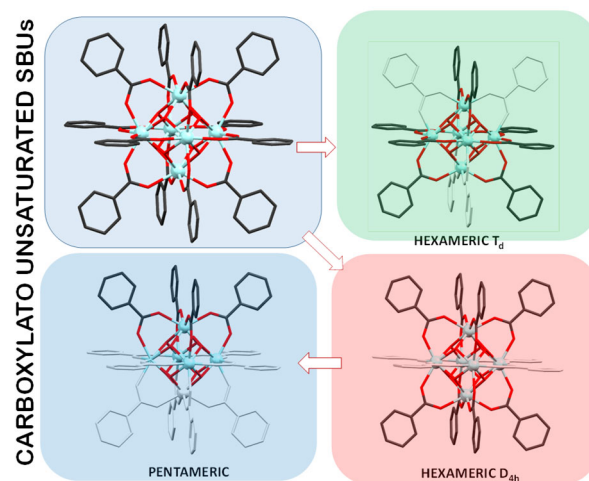


Figure 1. Species obtained and their relation with the $[\text{Zr}_6(\text{O})_4(\text{OH})_4(\text{OOCR})_{12}]$ fragment found in many MOFs (missing ligands: light grey).

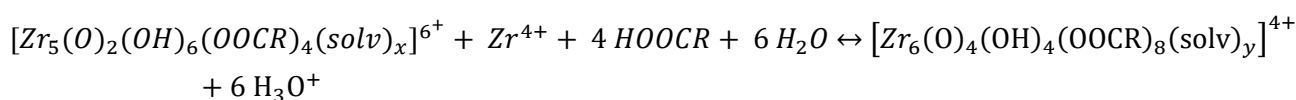
dropwise with water until pH \approx 0.0 (**2**), pH \approx 0.5 (**1**), or left at pH $<$ -0.2 (**5**). Colorless single-crystals appeared after four days.

$[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu\text{-OOC}\text{C}_6\text{H}_5\text{O})_8(\text{H}_2\text{O})_8]\text{Cl}_4 \cdot 28\text{H}_2\text{O}$ (**3**) and $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu\text{-OOC}\text{C}_6\text{H}_5\text{O})_8(\text{H}_2\text{O})_8]\text{Cl}_4 \cdot 27\text{H}_2\text{O}$ (**4**). A solution of 0.3870 g of ZrCl_4 dissolved in 4.8/0.2 mL of an ethanol/water solution was added dropwise to an 8 mL ethanol solution containing the corresponding ligand, 0.4586 g of 2-hydroxybenzoic acid for **3** or 3-hydroxybenzoic acid for compound **4**. The resulting colorless solution was basified dropwise with water until pH \approx 0.5 (**3**) or pH \approx 1.0 (**4**). Colorless single-crystals appeared after seven days.

$[\text{Zr}_5(\mu_3\text{-O})_2(\mu_3\text{-OH})_6(\mu\text{-OOC}\text{C}_6\text{H}_5)_4(\text{H}_2\text{O})_{11}(\text{PrOH})]\text{Cl}_6 \cdot 2\text{PrOH} \cdot 11\text{H}_2\text{O}$ (**6**). This compound was prepared mixing a solution of ZrCl_4 (0.3870 g) in 2.5/2.5 mL ethanol/propanol mixture and benzoic acid (0.4054 g) in 8 mL propanol. The resulting colorless solution was left at pH $<$ -0.2 and colorless single-crystals are formed four days later.

Results and Discussion

ESI+ mass spectra obtained for the ZrCl_4 /benzoic acid system at different very acidic pH conditions (0, 0.5 and 0.8) show two major signals centered at m/z 927 and 884 with a 0.5 spacing of the peaks indicative of 2+ charge states for both species. The molecular formula for the heavier signal agrees well with a $[\text{Zr}_6(\text{O})_4(\text{OH})_4]$ core where the number the benzoate anions attached to the cluster is reduced from the expected 12 (the well-known $[\text{Zr}_6(\text{O})_4(\text{OH})_4(\text{OOCR})_{12}]$ SBU found in many MOFs) to 8 providing a carboxylate-unsaturated entity. These hexameric species incorporates two additional hydroxide anions and solvent molecules complete the coordination sphere of the cluster. The signal at 884 has been assigned to a pentameric zirconium in which twelve solvent molecules, four benzoato ligands and four chlorides stabilize a $[\text{Zr}_5(\text{O})_2(\text{OH})_6]$ core. Both signals show modifications in their relative intensities as a function of the pH. The addition of water and subsequent dilution driven mild basification of the media results in a relative decrease of the intensity for the signal belonging to the pentameric species, whereas that related to the hexameric species increases considerably. This fact can be interpreted as an acid-base equilibrium between the two polynuclear species (Scheme 1).



Scheme 1. Acid-base equilibrium in the transformation between pentameric and hexameric species.

These species were isolated in the solid state and the crystal structures of chloride salts were determined. In hexameric (**1-4**) and pentameric (**5-6**) entities the hydroxide or oxide anions are positioned alternately in the center of each triangular face of the metal defining the square pyramid or octahedron. It means the hexameric entity has a $[\text{Zr}_6(\text{O})_4(\text{OH})_4]$ core whereas the pentamer shows a $[\text{Zr}_5(\text{O})_2(\text{OH})_6]$ core, in which the lack of a sixth zirconium atom implies that the four hydroxides pointing toward the vacant are not further polarized to produce the observed alternation of oxides/hydroxides of the triangular faces (Figure 2). The external coordination positions of the metal atoms are occupied by water molecules and carboxylato ligands. $\text{Zr-O}_{\text{oxide}}$ distances are always the shortest ones (2.00–2.14 Å), those involving the oxygen atoms of the carboxylato groups are between 2.16–2.28 Å, whereas those of hydroxides and water molecules are the longest ones with values between 2.18–2.37 Å. The distance between adjacent zirconium atoms is in the range of 3.47–3.54 Å. The positive charge of discrete entities are balanced by

chloride counterions which play a key role in directing the crystal packing. Ionic interactions are reinforced in **1–3** by strong hydrogen bonds established by chloride counterions and the bridging hydroxide anions located in half of the triangular faces of the octahedrally shaped hexameric entities ($d_{\text{OH}\cdots\text{Cl}}$: 2.97–3.26 Å). In **4**, the hydroxyl residues protruding from the hexameric entities provide a better placement for the chloride counterions to establish hydrogen bonding interactions. Six chloride counterions are present in **5** and **6**, but only three of them are strongly hydrogen bonded to the bridging hydroxide anions. In all compounds, solvent molecules account for a great portion of the total volume of the solid (21.9–33.3%) and their loss after the removal of the crystals from the mother liquid implies a transformation of the crystal structure.

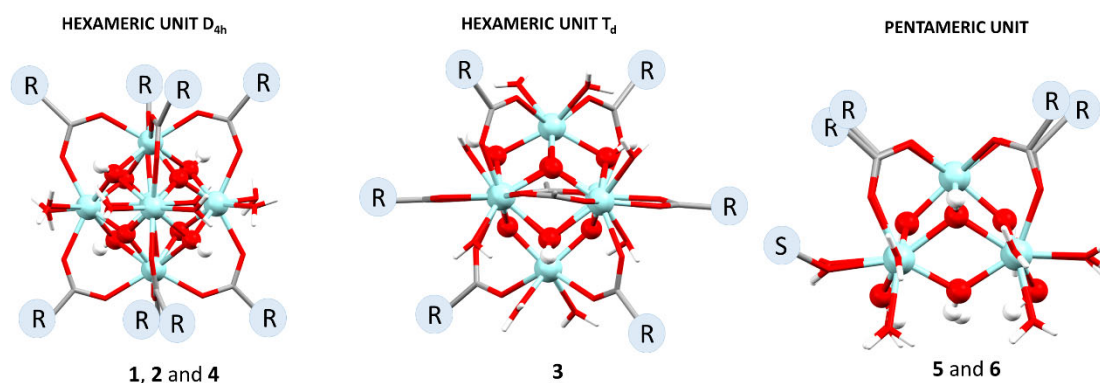


Figure 2. Polynuclear entities present in the compounds.

Conclusions

We have shown that there is plenty of chemistry still to be discovered about the first stages of the zirconium-carboxylate cluster formation. The results must be understood as frozen images along this process but also reveal the opportunities that arise from a fine control of the synthetic conditions. Small modifications of the pH of the media can considerably affect in the isolation of clusters with different nuclearity and carboxylate-ligand content. In addition, species with unsaturated carboxylate and/or metal positions can be a starting point to develop a richer chemistry by completing those vacancies with different carboxylic ligands or metal centers. Additionally, these highly positively charged polynuclear clusters are potential building blocks to prepare a plethora of ionic compounds by combining them with different counterions, providing some successful examples.⁴

References

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