The influence of water in the synthesis of Zr-based metal-organic framework UiO-66: isolation and reactivity of the new species [ZrCl(OH)$_2$(DMF)$_2$]Cl

Marco Taddei, Jeroen A. van Bokhoven and Marco Ranocchiari

1 Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland. Email: marco.ranocchiari@psi.ch
2 Institute for Chemical and Bioengineering, ETH Zürich, Vladimir Prelog Weg 1, 8093 Zürich, Switzerland
#Present address: Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, 56124, Pisa, Italy

Abstract

We recently discovered that aging a solution of zirconium(IV) tetrachloride (ZrCl$_4$) in $N$,$N$-dimethylformamide (DMF) in the presence of water, followed by addition of terephthalic acid linker, reduces the crystallite size of the metal-organic framework UiO-66 [Chem. Commun. 2016, 52, 6411-6414]. In an effort to shed light into the nature of the aging effect and on its relationship with the crystallite size of UiO-66, we report here the isolation and structural characterization of a microcrystalline zirconium-based compound of formula [ZrCl(OH)$_2$(DMF)$_2$]Cl, which is formed during the aging process. The Zr(IV) ions are coordinated by hydroxide, DMF and chloride to produce a one-dimensional polymer. Thanks to the presence of two –OH groups per zirconium atom, [ZrCl(OH)$_2$(DMF)$_2$]Cl is a suitable precursor for the synthesis of UiO-66 in dry DMF, affording a product having smaller crystallite size than that obtained from a reaction mixture having the same chemical composition, but using ZrCl$_4$ as the Zr(IV) source. By starting from ZrCl$_4$ and generating [ZrCl(OH)$_2$(DMF)$_2$]Cl in situ in solution through aging, we obtained smaller crystallites as the aging time increased, proving that [ZrCl(OH)$_2$(DMF)$_2$]Cl plays a role in the aging process. The possible role of [ZrCl(OH)$_2$(DMF)$_2$]Cl in the crystallization mechanism of UiO-66 is also discussed, with emphasis on its relationship with the amount of water in the reaction mixture.
**Introduction**

Zirconium-based metal-organic frameworks (Zr-MOFs), first reported in 2008,\(^1\) have taken the field of MOFs by storm, rapidly becoming one of the most intensely investigated families of compounds.\(^2\) This is mainly due to their superior thermal, chemical and mechanical stability, which is attributed to the combination of strong bonds between the carboxylic linkers and zirconium and the high degree of connectivity of the hexanuclear [Zr\(_6\)O\(_4\)(OH)\(_4\)]\(^{12+}\) clusters.\(^1,3\)\(^-\)\(^4\) One important feature of Zr-MOFs is that their crystallite size can be tuned to span over four orders of magnitude (from 10s of nm up to 100s of µm) by using crystallization modulators during synthesis.\(^5\)\(^-\)\(^10\) These modulators are usually either monocarboxylates that compete with the linker for coordination to the metal clusters (coordination modulators)\(^5\)\(^-\)\(^9\) or acidic species that inhibit deprotonation of the linker (protonation modulators).\(^10\) We recently reported that the crystallite size of UiO-66 can also be modulated by aging a solution of zirconium(IV) tetrachloride (ZrCl\(_4\)) in N\(_2\)N-dimethylformamide (DMF) at room temperature in the presence of different amounts of water and acetic acid, prior to introduction of terephthalic acid (H\(_2\)bdc) and heating.\(^11\)\(^-\)\(^12\) An important feature of the aging process, which distinguishes it from other modulation methods, is that it uses time as the modulation parameter. We had evidence that water is the main responsible for this effect, which we speculated to be primarily kinetic in nature and due to the formation of some pre-nucleation species more reactive than ZrCl\(_4\). Water plays a central role in the crystallization mechanism of Zr-MOFs, being necessary to provide the oxide and hydroxide groups that form the backbone of the hexanuclear clusters.\(^13\) The influence of water on the crystallization kinetics in DMF solvent of UiO-66 (based on H\(_2\)bdc as the linker)\(^14\) and Zr-fumarate (also known as MOF-801),\(^15\) respectively, was first investigated by *in-situ* energy dispersive X-ray diffraction (EDXRD). These two studies suggested that nucleation is the rate-determining step and that water accelerates the formation of Zr-MOFs inducing faster the nucleation, presumably by favoring hydrolysis of the zirconium precursor. Zirconium oxychloride octahydrate (ZrOCl\(_2\)\(\cdot\)8H\(_2\)O) promotes faster crystallization of the MOF than ZrCl\(_4\). This is arguably because the former precursor is constituted of [Zr\(_4\)(OH)\(_8\)(H\(_2\)O)\(_{16}\)]\(^{8+}\) tetramers,\(^16\) which are the product of hydrolysis of the latter precursor.
Combination of in-situ small and wide angle X-ray scattering (SAXS and WAXS, respectively), with the aid of a DFT-based metal-organic molecular orbital (MOMO) analysis, showed that the formation of crystalline UiO-66 occurs via an amorphous metastable phase containing superprotonated $[\text{Zr}_6(\text{OH})_8]^{16+}$ clusters already interconnected via the organic linkers, with extra-framework chloride species counterbalancing the excess positive charge. This intermediate step is followed by release of excess protons during the final step, leading to crystalline UiO-66. This proton release favours the condensation of further clusters and linkers to form the metastable phase, resulting in an autocatalytic process. The authors mention that “The rearrangement of such clusters [referring to the tetrameric species resulting from hydrolysis of ZrCl$_4$] into the hexanuclear UiO-66 building block follows an unknown path, but what is certain is that the pathway to condensation must be both water and acid catalysed, since in the appearance of $\mu_3$-O(H) bridges, O’s remain largely protonated”. This suggests, again, that water plays a role in the early stages of crystallization. Since 37% HCl in water was employed as a source of protons in this study, it is reasonable to assume that water also intervenes in the last step of the proposed mechanism, favouring shuttling of protons released from the $[\text{Zr}_6(\text{OH})_8]^{16+}$ clusters and therefore influencing the kinetics.

Further insight into the early stages of MOF formation recently came from in situ pair distribution function (PDF) analysis, which suggested that the hexanuclear secondary building units (SBUs) are already present in solution at room temperature when ZrCl$_4$ is dissolved in DMF in the presence of either water or 37% HCl in water. Upon addition of terephthalic acid to this solution, multinuclear clusters are formed, which then aggregate to grow crystallites of UiO-66. While the persistence of the SBUs could be indirectly presumed from synthetic reports where Zr$_6$ methacrylate or acetate oxoclusters were employed as precursors of Zr-MOFs in both solvothermal and mechanochemical conditions, direct evidence had been missing until the study of Xu et al. was published.

Besides the practical value of aging as a tool to control the crystallite size of the MOF, we recognize that a fundamental understanding of the aging process could also provide further precious insight into the early stages of crystallization, especially concerning the role of water. To this end, we report herein on the structural characterization of a Zr-based coordination
polymer, where Zr(IV) ions are coordinated by DMF, hydroxide and chloride ions, which was initially isolated in poorly crystalline form during an aging-modulated process. With this compound in hand, we performed a meticulous investigation aimed at understanding its role during the aging process and during crystallization of UiO-66.

**Experimental section**

*Materials*

ZrCl₄, 1,4-Benzenedicarboxylic acid (H₂bdc), ethanol, acetone and N,N-Dimethylformamide (DMF) were purchased from Sigma-Aldrich. ZrOCl₂·8H₂O was purchased from Merck Millipore. All reagents were used as received, except for DMF, which was treated as detailed in the following to remove traces of water.

*Preparation of dry DMF*

Dry DMF was prepared by flushing DMF through a column of basic alumina and collecting under a stream of argon in a round bottom Schlenk flask containing activated 3A molecular sieves.

*Preparation of HCl solution in dry DMF (HCl/DMF)*

A solution of HCl in dry DMF was prepared by bubbling gaseous HCl in the solvent, according to the following procedure: a three neck, 250 mL round bottom flask was loaded with NaCl (15 g) and equipped with a dropping funnel, loaded with 98% H₂SO₄ (20 mL), on the central neck. One side neck was connected to a Schlenk line, whilst the other one was connected to a trap containing 98% H₂SO₄, which was in turn connected to a second trap containing dry DMF (20 mL). A third trap, containing a solution of NaOH in water, was placed at the end of the setup to neutralize excess HCl. H₂SO₄ was added dropwise to NaCl under a stream of Ar for 30 minutes. Titration of the resulting HCl/DMF solution, diluted 1:9 with water, with 0.1 M NaOH gave a concentration of 3.2 M.

*Synthesis of [ZrCl(OH)₂(DMF)₂]Cl*
ZrCl$_4$ (466 mg, 2 mmol) was placed in a 20 mL glass vial and dissolved in dry DMF (10 mL) and water (144 µL, 8 mmol). The vial was sealed with a cap equipped with polytetrafluoroethylene (PTFE) septum and incubated at 60 °C for 24 hours. The white solid formed was recovered by centrifugation, washed with DMF (20 mL) and ethanol (20 mL), and dried in a vacuum oven at 60 °C. Yield: 563 mg (87%, based on Zr).

Elemental analysis: Experimental (calculated): C = 20.5% (21.0%); H = 4.7% (4.7%); N = 8.1% (8.2%); Cl = 20.1% (20.7%).

In an alternative procedure, ZrOCl$_2$·8H$_2$O (322 mg, 1 mmol) was placed in a 20 mL glass vial and dissolved in dry DMF (10 mL). The vial was sealed with a cap equipped with PTFE septum and incubated at 60 °C for 24 hours. The white solid formed was recovered by centrifugation, washed with DMF (20 mL) and ethanol (20 mL), and dried in a vacuum oven at 60 °C. Yield: 288 mg (84%, based on Zr).

**Synthesis of UiO-66 starting from [ZrCl(OH)$_2$(DMF)$_2$]Cl as precursor**

[ZrCl(OH)$_2$(DMF)$_2$]Cl (342 mg, 1 mmol) was placed in a 40 mL glass vial and dissolved in dry DMF (20 mL) by heating at 80 °C for 30 min. The mixture was left to cool and water (36 µL, 2 mmol) and/or HCl/DMF (63 µL, 2 mmol) were added, depending on the chosen synthesis conditions (see Table 1 for details). Finally, H$_2$bdc (166 mg, 1 mmol) was added, the vial was sealed with a cap equipped with PTFE septum and incubated either at 90 °C for 96 h or at 120 °C for 24 h. The white solid obtained was centrifuged, washed in DMF (2 × 20 mL) and in acetone (2 × 20 mL) and then dried in a vacuum oven at 60 °C.

Yields: 190 mg (90 °C, no additives); 221 mg (90 °C, 2 eq H$_2$O); 87 mg (90 °C, 2 eq HCl); 268 mg (90 °C, 2 eq H$_2$O, 2 eq HCl); 223 mg (120 °C, no additives); 203 mg (120 °C, 2 eq H$_2$O); 133 mg (120 °C, 2 eq HCl); 242 mg (120 °C, 2 eq H$_2$O, 2 eq HCl).

**Synthesis of UiO-66 starting from ZrCl$_4$ as precursor**

ZrCl$_4$ (233 mg, 1 mmol) was placed in a 40 mL glass vial and dissolved in dry DMF (20 mL) and water (36 µL, 2 mmol). H$_2$bdc (166 mg, 1 mmol) was added, the vial was sealed with a cap equipped with PTFE septum and incubated either at 90 °C for 96 h or at 120 °C for 24 h. The
white solid obtained was centrifuged, washed in DMF (2 × 20 mL) and in acetone (2 × 20 mL) and then dried in a vacuum oven at 60 °C. Yields: 285 mg (90 °C); 206 mg (120 °C).

Synthesis of UiO-66 in the presence of [ZrCl(OH)$_2$(DMF)$_2$]Cl generated in situ

ZrCl$_4$ (466 mg, 2 mmol) was placed in a 20 mL glass vial and dissolved in dry DMF (10 mL) and water (144 μL, 8 mmol). The vial was sealed with a cap equipped with PTFE septum and incubated at 60 °C for either 0, 1 or 2 h. Following this pretreatment, H$_2$bd (166 mg, 1 mmol) was added, the vial was sealed with a new cap equipped with PTFE septum and incubated at 120 °C for 24 h. The white solid obtained was centrifuged, washed in DMF (2 × 20 mL) and in acetone (2 × 20 mL) and then dried in a vacuum oven at 60 °C. Yields: 778 mg (no aging); 812 mg (1h aging); 743 mg (2h aging).

Analytical procedures

Powder X-ray diffraction (PXRD) patterns for qualitative purposes were collected in the 4-40° 2θ range with a Bruker D8 Advance diffractometer working in Bragg-Brentano geometry and equipped with a LYNXEYE XE detector, using the Cu Kα radiation. The X-ray tube was operated at 40 W and 40 mA.

Nitrogen sorption isotherms at 77 K were measured on a Micromeritics Tristar II analyzer. The samples (about 30-50 mg) were activated overnight under vacuum at 150 °C prior to analysis. The BET equation was fitted in the 0.010-0.070 P/P$_0$ range.

Transmission electron microscopy (TEM) samples were prepared by dispersing the material in ethanol and putting some drops of this suspension onto the TEM grid (C-foil on Cu grid). TEM was performed on a Tecnai F30 (FEI, USA) microscope operated at 300 kV (field emission gun; SuperTwin lens with a point resolution of ca. 2 Angstrom).

Thermal gravimetric analysis (TGA) was performed on a Mettler-Toledo instrument at a 5 °C min$^{-1}$ heating rate up to 700 °C under 80:20 nitrogen/oxygen atmosphere.

Elemental analysis (CHN) was performed on a LECO Truspec Micro instrument. Cl content was determined by Schöniger oxidation, followed by ion chromatography.
Structure solution and refinement.

A high resolution PXRD pattern of $[\text{ZrCl(OH)}_2(\text{DMF})_2]\text{Cl}$ was collected at the Material Science (MS) beamline at Swiss Light Source (SLS), using 16 keV radiation. The powder was loaded in a glass capillary having outer diameter of 0.5 mm and data were collected in the $3.2 - 45.0^\circ$ 2θ range with a 0.0032° 2θ step size. Si-640d reference sample was employed as a standard to refine the wavelength and zero error. Indexing was performed using the TOPAS 5.0 program, identifying a triclinic unit cell as the most probable solution. Whole powder pattern fitting, performed by the Pawley method using the same program, confirmed the triclinic structure. Structure solution was performed using the real space global optimization methods implemented in the FOX program by using the parallel tempering algorithm. A reliable structural model was generated when the asymmetric unit contained a fragment, composed of one Zr atom bound to two DMF molecules and two O atoms, and two Cl atoms, one of which was located at coordination distance from Zr. Rietveld refinement of the obtained structural model was performed using the program TOPAS 5.0. First, a Pawley refinement was carried out to model background, profile shape parameters (CS_L, CS_G, Strain_L, Strain_G) and lattice parameters ($a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$). Then, Rietveld refinement was performed to model the atomic coordinates and atomic displacement parameters (the input file used for this refinement is available as supporting information). Six Zr-O and one Zr-Cl distance restraints were used to refine the coordination geometry around the Zr atom, while five distance restraints (C-N, C-O) and four angle restraints were employed to define the geometry of each DMF fragment. The isotropic atomic displacement parameter for Zr was refined independently, while those of the light atoms were constrained to have the same value. At the end of the refinement, all the parameters were refined together until convergence. Crystal data and details of the refinement are reported in Table S1. Figure S1 shows the final Rietveld and difference plots. The input file used for Rietveld refinement is also included as Supporting Information.

Results and discussion

Synthesis and crystal structure of $[\text{ZrCl(OH)}_2(\text{DMF})_2]\text{Cl}$
During our previous study on the aging effect on the synthesis of UiO-66, we observed formation of a poorly crystalline solid (Figure S2) upon aging for 24 h of a 0.15 M solution of ZrCl₄ in DMF in the presence of 24 equivalents (eq) of water. By carefully tuning the reaction conditions using a 0.2 M solution of ZrCl₄, 4 eq. of water followed by heating at 60 °C for 24 h, the solid could be obtained in microcrystalline form, suitable for structure solution from synchrotron PXRD data (Figure S3). Chemical analysis of the solid, combined with TGA (Figure S4), suggested the formula [ZrCl(OH)(DMF)₂]Cl. Figure 1 and Figure S5 show its crystal structure. [ZrCl(OH)(DMF)₂]Cl crystallizes in the triclinic space group P-1, with lattice parameters a = 6.7822(2) Å, b = 9.6051(2) Å, c = 10.6748(2) Å, α = 75.775(2) °, β = 84.364(4) °, γ = 82.006(3) °. [ZrCl(OH)(DMF)₂]Cl is a one-dimensional polymer based on heptacoordinated Zr atoms connected by bridging μ₂–OH groups along the a axis. Each Zr atom is coordinated in a pentagonal bipyramid fashion to four μ₂-OH groups occupying four equatorial positions (Zr–O distances ranging between 1.953 Å and 2.385 Å), two O atoms belonging to two crystallographically independent DMF molecules - occupying one equatorial (Zr–O distance = 1.996 Å) and one axial position (Zr–O distance = 2.059 Å), respectively - and one Cl atom occupying one axial position (Zr–Cl distance = 2.421 Å) (Figure S6). The residual positive charge on each Zr atom is counterbalanced by one extraframework Cl⁻ ion, located at hydrogen bonding distance from two -OH groups (Cl–O distances = 3.060 Å and 3.077 Å, respectively). No evident interactions seem to exist between adjacent chains.

Figure 1. View of the crystal structure of [ZrCl(OH)(DMF)₂]Cl. Color code: Zr, pink; Cl, green; O, red; N, blue; C, gray. Hydrogen bonds are represented as red dashed lines.
The effect of the acidity of the reaction medium on the formation of \([\text{ZrCl(OH)}_2(\text{DMF})_2]\text{Cl}\) was investigated by performing syntheses starting from 0.1 M ZrCl\(_4\) at 60 °C in the presence of either 2 eq of dry HCl or 2 eq of triethylamine, alongside 7 eq of water. Addition of HCl inhibits the formation of solid product, even upon heating to 100 °C, whereas triethylamine affords a larger amount of a slightly less crystalline product than the experiment with no additives (Figure S7, Table S2). We explain this behavior by noting that deprotonation of water is needed to afford the \(-\text{OH}\) groups that bridge Zr atoms and enable propagation of the polymeric chain of \([\text{ZrCl(OH)}_2(\text{DMF})_2]\text{Cl}\), a process that is promoted by the addition of a base and inhibited by an acid.

Solid \([\text{ZrCl(OH)}_2(\text{DMF})_2]\text{Cl}\) can be dissolved in DMF up to a concentration of 0.05 M by heating to 80 °C. It is highly soluble in water at room temperature, in methanol (up to 0.04 M at room temperature) and in acetic acid (up to 0.03 M at 80 °C), whereas it is insoluble in acetonitrile, ethanol and tetrahydrofuran, even upon heating. Given its polymeric nature, we presume that the dissolution process likely has a reactive nature and involves coordination of polar solvents to Zr, leading to deconstruction of long polymeric chains into smaller fragments.

\([\text{ZrCl(OH)}_2(\text{DMF})_2]\text{Cl}\) can be synthesized starting from either ZrCl\(_4\) or ZrOCl\(_2\)-8H\(_2\)O, suggesting that it is a thermodynamically favored species when Zr\(^{4+}\), Cl\(^-\) and H\(_2\)O are present at the same time and in nearly stoichiometric amounts in a DMF solution. It is worth to note here that the crystal structures of ZrCl\(_4\) and ZrOCl\(_2\)-8H\(_2\)O are very different. ZrCl\(_4\) is a one-dimensional polymer, where Zr atoms are octahedrally coordinated and connected through bridging Cl atoms (Figure S8).\(^{28}\) ZrOCl\(_2\)-8H\(_2\)O is a fully hydrolyzed and discrete tetramer of formula \([\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]\text{Cl}_8(\text{H}_2\text{O})_{12}\), where Zr atoms are octacoordinated and connected through bridging \(-\text{OH}\) groups, and no Zr-Cl bonds exist (Figure S9).\(^{16}\) This suggests that DMF, water and Cl\(^-\) all play an active coordinating role towards Zr(IV) in solution. This is not surprising for either water or DMF, given the large literature dealing with coordination compounds of Zr(IV) involving these two species.\(^{29-36}\) However, Cl\(^-\) is reported to be a weak coordinating species for Zr(IV) in aqueous solvent, and its ability to bind to Zr(IV) in DMF is most likely due to the lower polar character and weaker coordinating ability of this organic solvent, if compared to water.\(^{29}\)
[ZrCl(OH)$_2$(DMF)$_2$]Cl as a precursor for UiO-66

Given that [ZrCl(OH)$_2$(DMF)$_2$]Cl is a partially hydrolyzed Zr(IV) species and contains 2 eq of O per Zr atom, we speculated that it could be a precursor for the synthesis of UiO-66, whose [Zr$_6$O$_4$(OH)$_4$]^{12+} clusters require only 1.33 eq of O per Zr atom. Reaction of 1 mmol of [ZrCl(OH)$_2$(DMF)$_2$]Cl and 1 eq of H$_2$bdc in 20 mL of dry DMF at 90 °C for 96 h led to formation of a UiO-66 phase, as evidenced by PXRD analysis (Figure 2). The full width at half maximum (FWHM) of the (111) reflection, located at 7.3° 2θ, is 0.317° (Table 1). The relatively intense background at low angle hints at diffuse scattering due to the possible presence of amorphous matter. TEM analysis shows no well-defined morphology of the solid, with no single crystallites visible (Figure 3). TGA displays a relatively small weight loss above 400 °C, where framework decomposition occurs, which might suggest that the MOF is highly defective (Figure S10). However, the presence of amorphous matter, especially if of low organic content, could affect the accuracy of the weight loss estimation. This is apparently confirmed by N$_2$ sorption analysis, which reveals a surface area of 634 m$^2$ g$^{-1}$ - much lower than that reported for defect-free UiO-66 (1105 m$^2$ g$^{-1}$) and presence of hysteresis at relative pressure above 0.4, indicative of condensation of N$_2$ within interparticular meso- and macropores, typical of a MOF with very small crystallite size (Table 1, Figure S11). Addition of 2 eq of water to the reaction mixture yields a very similar result, in terms of yield and properties of the MOF (Figures 2-3, Table 1, Figures S10-11). Addition of 2 eq of dry HCl in DMF leads instead to the formation of a phase having FWHM (111) of 0.226°, suggesting that larger crystallites were grown (Figure 2, Table 1). TEM analysis displays again no well-defined morphology, although single crystallites with size of about 20 nm can be distinguished (Figure 3). TGA suggests that this product is either less defective or contains less amorphous matter (Figure S10). N$_2$ sorption analysis supports the latter, revealing an increased surface area of 874 m$^2$ g$^{-1}$ and the presence of small hysteresis at relative pressure above 0.5, again indicative of condensation of N$_2$ within interparticular meso- and macropores (Table 1, Figure S11). The yield of the synthesis in the presence of HCl is much lower than in the case where no additive was used (87 mg vs 190 mg, respectively). This evidence, along with the larger crystallite size of the product, suggests that HCl slows down the crystallization rate, most likely acting as a protonation modulator, as already seen during the
synthesis of [ZrCl(OH)$_2$(DMF)$_2$]Cl. In addition, the lower yield suggests that HCl could also prevent formation of considerable amounts of amorphous matter. Combined addition of 2 eq of water and 2 eq of HCl affords a solid with similar crystallite size and textural properties to that prepared using only HCl as an additive, but in much higher yield (Figures 2-3, Table 1, Figures S10-11). This suggests that the protonation modulation effect of HCl is retained, but the presence of water – in addition to the -OH groups already present in [ZrCl(OH)$_2$(DMF)$_2$]Cl – is crucial in allowing faster formation of the MOF. Given that water alone does not exert any significant effect on the process, we speculate that, when in combination with HCl, water might enable more efficient proton transport, thus favoring the autocatalytic process recently described by Goesten et al.\textsuperscript{17} Broad superlattice reflections, indicative of the presence of ordered nanodomains of missing-cluster defective unit cells with reo topology,\textsuperscript{40} appear at low 2θ angle and at around 10° 2θ (Figure 2). An analogous trend was observed when the syntheses were carried out at 120 °C for 24 h (Table S3, Figures S12-15). At higher temperature, broader PXRD peaks are consistently obtained, suggesting that increasing the temperature leads to higher nucleation rate and formation of smaller crystallites, in agreement with previous observations.\textsuperscript{14-15}

![Figure 2. PXRD patterns of UiO-66 prepared reacting [ZrCl(OH)$_2$(DMF)$_2$]Cl and H$_2$bdc in dry DMF at 90 °C for 96 h in the presence of no additive (black line), 2 eq of water (red line), 2 eq of HCl (blue line), 2 eq of water and 2 eq of HCl (olive line).]
Figure 3. TEM images of the products of syntheses starting from [ZrCl(OH)(DMF)₂]Cl with no additive (a), addition of 2 eq of water (b), addition of 2 eq of HCl (c), addition of 2 eq of water and 2 eq of HCl (d) and starting from ZrCl₄ with addition of 2 eq of water (e). All syntheses performed at 90 °C for 96 h.

Table 1. Results of UiO-66 syntheses performed at 90 °C for 96 h employing either [ZrCl(OH)(DMF)₂]Cl or ZrCl₄ as precursors.

<table>
<thead>
<tr>
<th>Zr source</th>
<th>Additive</th>
<th>Yield (mg)</th>
<th>FWHM (111) (°)</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ZrCl(OH)(DMF)₂]Cl</td>
<td>-</td>
<td>190</td>
<td>0.317</td>
<td>634</td>
</tr>
<tr>
<td>[ZrCl(OH)(DMF)₂]Cl</td>
<td>H₂O, 2 eq</td>
<td>221</td>
<td>0.307</td>
<td>609</td>
</tr>
</tbody>
</table>
Role of [ZrCl(OH)$_2$(DMF)$_2$]Cl in the aging process

Once proved that [ZrCl(OH)$_2$(DMF)$_2$]Cl is in fact a suitable precursor for UiO-66 synthesis, we shifted our attention to investigating its potential involvement in the aging process to yield small UiO-66 nanoparticles. To this purpose, we synthesized UiO-66 starting from 0.05 M ZrCl$_4$ in dry DMF, in the presence of 2 eq of water and 1 eq of H$_2$bdc, at 90 °C for 96 h. The product of this synthesis was compared with that obtained starting from 0.05 M [ZrCl(OH)$_2$(DMF)$_2$]Cl in the presence of 2 eq of HCl, on the basis that the chemical composition of the reaction mixture is the same in the two cases and the possible differences would only be due from the different nature of the Zr source. PXRD analysis shows that ZrCl$_4$ affords a product with sharper Bragg reflections (Figure 4, Table 1), indicative of larger crystallites. Superlattice reflections are also clearly visible, hinting at the presence of defects. TEM clearly displays that these crystallites have round morphology and approach 100 nm in size (Figure 3). The weight loss above 400 °C, as revealed by TGA, is comparable, but a larger amount of solvent is removed from the framework at lower temperature, suggesting that this solid is more porous (Figure S10). This is corroborated by N$_2$ sorption analysis at 77 K, which reveals a surface area of 1087 m$^2$ g$^{-1}$ and a nearly perfect type 1 isotherm (Table 1, Figure S11). Analogous results were obtained when the synthesis was carried out at 120 °C for 24 h (Table S4, Figures S12-16). These observations, combined with the much higher yield obtained when ZrCl$_4$ is employed as Zr(IV) source – 285 mg vs 87 mg when starting from [ZrCl(OH)$_2$(DMF)$_2$]Cl – indicate that the crystallization process occurs with different kinetics and possibly following different paths, depending on the nature of the Zr(IV) source. When ZrCl$_4$ was reacted with H$_2$bdc at 120 °C with no additives, or in the presence of 2 eq of HCl, a very small amount (< 10 mg) of a poorly crystalline phase, vaguely resembling MIL-140A, was recovered (Figure S17), confirming that water is indeed essential for
the formation of the hexanuclear Zr clusters found in UiO-66, in agreement with the recent observations by Butova et al.\textsuperscript{13}

![Figure 4. PXRD patterns of UiO-66 prepared reacting [ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl and H\textsubscript{2}bdc in dry DMF at 90 °C for 96 h in the presence of 2 eq of HCl (black line) and reacting ZrCl\textsubscript{4} and H\textsubscript{2}bdc in dry DMF at 90 °C for 96 h in the presence of 2 eq of water (red line).](image)

The systematically smaller size of crystallites formed when [ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl is used as a precursor suggests that this species could in fact be involved in the aging process. Further demonstration of this was explored by reacting a 0.2 M solution of ZrCl\textsubscript{4} in dry DMF with 4 eq of water – either fresh or after incubation at 60 °C for one or two hours – and 1 eq of H\textsubscript{2}bdc at 120 °C for 24 h. Products with progressively broader Bragg reflections, indicative of smaller crystallites, are obtained when the linker is added after aging of the Zr solution (Figure 4, Table S4). The yields are comparable, in agreement with our previous work, where it was observed that aging does not significantly affect the yield of the reaction.\textsuperscript{11} Since [ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl is known to form when a solution with such composition is incubated at 60 °C, this experiment nicely confirms that [ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl plays a role during the aging process. Interestingly, if the same synthesis is carried out in the presence of 2 eq of HCl, the PXRD patterns of the products look basically identical (Figure S18). Having previously proven that HCl inhibits the formation of [ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl, we believe that this is further proof in support of the involvement of [ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl in the aging process.
Figure 5. PXRD patterns of UiO-66 prepared by reacting H$_2$bdc at 120 °C for 24 h with a fresh solution of ZrCl$_4$ 0.2 M in dry DMF with 4 eq of water (black line), with the same solution incubated for 1 h at 60 °C before addition of H$_2$bdc (red line) and incubated for 2 h at 60 °C before addition of H$_2$bdc (olive line).

Role of [ZrCl(OH)$_2$(DMF)$_2$]Cl in the crystallization of UiO-66

Having demonstrated that [ZrCl(OH)$_2$(DMF)$_2$]Cl is involved in the aging process, we asked ourselves whether we could have identified a potential intermediate in the crystallization process of UiO-66. Given that [ZrCl(OH)$_2$(DMF)$_2$]Cl can also be synthesized starting from ZrOCl$_2$·8H$_2$O – and that the aging effect is observed when the latter is used as a precursor (Figures S19-20) – we can infer that the aging process does not simply consist of a pre-hydrolysis of the Zr(IV) precursor, which makes it more reactive towards formation of the MOF, but it is rather a reaction path, common to different Zr(IV) precursors with different degrees of hydrolyzation, that generates a specific chemical species. However, [ZrCl(OH)$_2$(DMF)$_2$]Cl cannot be isolated when ZrCl$_4$ in dry DMF is reacted with 1 eq of H$_2$bdc and 4/6 eq of water at 60 °C and that the only solid product obtained in these syntheses is UiO-66 (Figures S21 and S22).

We can envision two potential scenarios: 1) [ZrCl(OH)$_2$(DMF)$_2$]Cl is an intermediate species in the crystallization process of UiO-66, which readily reacts with H$_2$bdc to yield UiO-66 after its formation, thus never reaching the solubility limit. 2) The presence of H$_2$bdc since the beginning of the reaction drives crystallization of UiO-66 through a different path, completely preventing
formation of $\text{[ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl}$. Either the formation of $\text{[ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl}$ is a rate determining step in the crystallization of UiO-66, and the aging process is a kinetic effect that drives the system past this step leading to formation of smaller crystallites than when $\text{ZrCl}_4$ is used as a precursor (1), or the aging process is a side reaction path undertaken only when there is no $\text{H}_2\text{bdc}$ in the system and the aging process has an influence not only on the kinetics of crystallization, but also on the thermodynamics (2).

$\text{Zr(IV)}$ is well known to have a very complex coordination chemistry in aqueous environment, forming a wide range of oligomeric and polymeric structures where -OH groups play a key role in bridging two or more Zr atoms.\textsuperscript{29-31} A similarly complex chemistry could take place in DMF medium and $\text{[ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl}$ could be only one of several species existing in solution and containing DMF, water and chloride as coordinating groups to zirconium. Since $\text{[ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl}$ can be isolated as a solid in high yields, there is a strong thermodynamic drive associated with its formation in the reaction conditions investigated here. The recent total scattering study by Xu et al.\textsuperscript{18} hints at the existence of $\text{Zr}_6$ clusters already in 0.2 M $\text{ZrCl}_4$ solutions in DMF in the presence of either $\text{H}_2\text{O}$ or concentrated HCl. However, Xu et al. added either 29 eq of pure $\text{H}_2\text{O}$ or 36 eq of $\text{H}_2\text{O}$ in the system in the form of a concentrated HCl solution, while we worked with almost stoichiometric amounts of water. We attempted the synthesis of $\text{[ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl}$ starting from 0.2 M $\text{ZrCl}_4$ in the presence of 32 eq of water, observing no formation of solid. Given the high solubility of $\text{[ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl}$ in water, we can deduce that, when a large excess of water is added, it never reaches its solubility limit in the reaction environment and that the hydrolysis rate is massively increased, pushing the system towards fast formation of $\text{Zr}_6$ oxy-hydroxy clusters, which are also soluble in the reaction medium. This suggests that the distribution of species existing in solution is strongly dependent on the amount of water and that $\text{[ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl}$ could in fact play a role in nucleation in the presence of stoichiometric water.

**Conclusion**

We have reported the synthesis and structural characterization of a microcrystalline Zr-based compound of formula $\text{[ZrCl(OH)\textsubscript{2}(DMF)\textsubscript{2}]Cl}$, where Zr ions are coordinated by hydroxide, DMF.
and chloride to produce a one-dimensional polymer. The compound was initially obtained in poorly crystalline form during aging for 24 h of a 0.15 M solution of ZrCl$_4$ in DMF in the presence of 24 eq of water. Upon optimization of the reaction conditions, [ZrCl(OH)$_2$(DMF)$_2$]Cl could be obtained in good crystallinity and high yield starting from both ZrCl$_4$ and ZrOCl$_2$·8H$_2$O in dry DMF as a solvent, suggesting that it is a thermodynamically favored product when Zr, water and chloride are present at the same time and in stoichiometric amounts in DMF. We demonstrated that [ZrCl(OH)$_2$(DMF)$_2$]Cl is a precursor of metal-organic framework UiO-66 in dry DMF and that it systematically affords a product having smaller crystallite size than that obtained from ZrCl$_4$ in the same conditions. Finally, we proved the involvement of [ZrCl(OH)$_2$(DMF)$_2$]Cl in the aging process by generating it in situ, obtaining smaller crystallites as the aging time increases. The possible role of [ZrCl(OH)$_2$(DMF)$_2$]Cl in the crystallization mechanism of UiO-66 was also discussed: the evidence that the presence of H$_2$bdc in the reaction mixture prevents precipitation of [ZrCl(OH)$_2$(DMF)$_2$]Cl suggests that it may be a highly reactive intermediate accessible only in the absence of the linker. We propose that further investigation into the coordination chemistry taking place in solution at different H$_2$O/Zr ratios is needed to gather further insight into mechanistic aspects.

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