

Zirconium-Formate Macrocycles and Supercage: Molecular Packing versus MOF-like Network for Water Vapor Sorption

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Supporting Information

ABSTRACT: In systematic efforts toward a new type of molecule-based porous materials, facile and efficient synthetic methods have been established to obtain macrocyclic $[Zr_6]_6$ and supercage-like $\{[Zr_6]_6\}_8$, where $[Zr_6]$ represents $[Zr_6O_4(OH)_4(CO_2)_n]$ building unit commonly found in Zrbased metal-organic frameworks. The reactions involve in situ hydrolysis of DMF solvent to produce formate linkers and thus do not require any organic ligand. A minor variation in the composition of two cyclic hexamers thus obtained results in dramatic differences in crystal packing which in turn lead to distinctive and selective sorption behavior for water vapor. It is shown that the high heat of water adsorption and



unrestricted uptake under high humidity are consequences of the highly polar surface and flexible crystal packing. The reversibility of water adsorption is demonstrated by cyclic measurements of uptake and regeneration under dynamic flow conditions.

INTRODUCTION

Development of research on metal-organic frameworks (MOFs) into functional porous materials for practical applications, such as storage and separation,¹ heterogeneous catalysis² and etc.,³ has depended critically on the usability of simple organic building blocks in a facile one-pot synthesis. Therefore, it is not surprising that some of the most intensely studied MOFs, for examples, MOF-5,⁴ HKUST-1,⁵ MIL-101,⁶ ZIF-8,⁷ MOF-74 (or CPO-27),⁸ and UiO-66,⁹ are all based on organic linkers that are not larger than the size of one phenylene unit.

One of the smallest organic linkers that can be used to build porous MOFs is formate (HCO2⁻).¹⁰ The four-atom monoanionic linker is known to adopt various coordination modes thanks to the smallest possible side group on the carboxylate carbon. Another interesting feature of formate as an organic linker is that it can be conveniently derived in situ from the hydrolysis of amide-based solvents such as DMF or DEF during the solvothermal synthesis of MOFs. In fact, porous manganese-formate, the seminal MOF reported by K. Kim and co-workers in 2004,¹¹ had initially been discovered serendipitously from the solvothermal reactions of Mn(II) salt in DEF.

Our group has been interested in polyoxotitanate clusters as potential building blocks for novel MOFs, and has recently reported that some of Ti-oxo-carboxylate clusters are porous molecular solids by themselves and can selectively and reversibly adsorb CO2.¹² In a natural extension of those studies, we set out investigations on Zr-carboxylate clusters

and were inspired by the persistence and stabilities of $[Zr_6O_4(OH)_4(CO_2)_{12}]$ secondary building unit in UiO-type MOFs originally reported by Lillerud et al.9 Therefore, we decided to pursue new synthetic routes for porous Zr carboxylates including formate. Our synthetic strategy has been to replace the commonly used monocarboxylic acid modulator¹³ with an inorganic acid that can also facilitate the hydrolysis of DMF. It was then noticed that highly crystalline materials form when ZrCl₄, in the absence of any organic ligand, is heated in DMF only with an aqueous acid. Therefore, the reaction parameters have been systematically varied to derive the products as apparently single crystalline phases. Hereby we report two novel phases of zirconium-formate clusters which could be referred as a macrocyclic molecule and MOF-like network solid, respectively, and their water vapor sorption properties measured under both static and dynamic flow conditions.

RESULTS AND DISCUSSION

According to our results optimized after screening out synthetic parameters such as metal/acid ratio, cosolvent, temperature, and an additive, if necessary, two closely related but structurally distinct phases of zirconium-formate (ZF hereafter) can be obtained in highly crystalline forms. The two compounds, $[Zr_{36}O_{24}(OH)_{52}(HCO_2)_{44}] \cdot 4[H_2N(CH_3)_2Cl]$ (ZF-2) and $[Zr_{36}O_{24}(OH)_{48}(HCO_2)_{48}]$ ·3KCl (ZF-3) are

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solvothermally synthesized in high yields using only hydrochloric and nitric acid, respectively, in DMF-CH₃CN solution of ZrCl₄. For ZF-3, an extra source of cation, such as K⁺, is needed to warrant the phase purity and high yields. The formation of ZF-2 is not affected by the addition of inorganic salt as far as hydrochloric acid is used as the hydrolysis medium. The same is true for the addition of organic modulator which only affect the crystal habits of the product. We note that direct reactions between ZrCl₄ and formic acid or formate do not yield ZFs and instead result in the buildup of pressure inside the reaction vessel. It appears that the slow release of formic acid from DMF through hydrolysis is essential for the successful synthesis. ZF-2 and -3 are somewhat soluble in water probably because of the salt in the crystal structure but insoluble and stable indefinitely in common organic solvents.

As shown by the X-ray powder diffraction (XRPD) patterns in Figure 1, as-synthesized ZF-2 and -3 are not only highly



Figure 1. Experimental and simulated X-ray powder diffraction patterns for as-synthesized ZF-2 and -3.

crystalline, but also their bulk phases are crystallographically pure judging from the comparison between experimental and theoretical diffraction patterns based on single-crystal analysis (see below).

X-ray diffractions on large, polyhedral single crystals of ZF-2 reveal that it has a cyclic molecular structure composed of six $[Zr_6O_4(OH)_4]$ units supported by formate ligands (Figure 2a). The [Zr₆] units in the cyclic hexamer are interconnected by four sets of μ -OH linkers and two sets of mixed μ -OH/HCO₂ linkers. Due to the different lengths of the two types of μ_2 linkers, the molecule assumes an ellipsoidal shape measuring $2.6 \times 2.2 \text{ nm}^2$, and is slightly bent when viewed from its side. The μ_3 -O and μ_3 -OH groups within the [Zr₆] unit are clearly discernible based on interatomic distances and angles. The nature of μ_2 -oxygen bridges between [Zr₆] units is established based on the bond-valence sum (BVS) analysis.¹⁴ The BVS values of the μ_2 -oxygen atoms are in the range 0.98–1.16, and strongly suggest that the bridging ligands are all hydroxo, not oxo groups. With unambiguous assignments of charges on HCO_2^{-} linkers and Zr(IV) ions, the macrocyclic hexamer itself is thus charge-neutral. In the crystal structure, however, four Cl^{-} ions are found for every $[Zr_{36}]$ cluster at the outer rim of the macrocycle bonded through hydrogen atoms of μ_3 - and μ_2 -



Figure 2. (a) X-ray structure of the molecule of ZF-2. (b) Packing structure viewed along b axis in the crystal. Color code: green Zr, red O, gray C, white H, and orange Cl.

OH groups (Figure 2b). The extra charges are balanced by dimethylammonium cations derived apparently from DMF solvent. Although the cation could not be located from the single crystal data due to disorders in large intermolecular voids, its presence has been verified by FT-IR (Figure S1 of the Supporting Information, SI) and ¹H NMR spectra (Figure S5) and nitrogen contents in elemental analysis.

In the face-centered orthorhombic lattice of ZF-2, the bowlshaped molecules simply pack in an alternating brick-wall pattern, as shown in Figure 2b, and the intermolecular voids are filled by disordered solvent molecules. The closest contacts between adjacent hexameric cycles are van der Waals interactions involving the formate groups and hydrogen bonding mediated by lattice water molecules.

ZF-3 crystallizes in the cubic space group $I\overline{4}3m$, and also is a cyclic hexamer of $[Zr_6O_4(OH)_4]$ units supported by formate ligands (Figure 3a).

Unlike the molecule of ZF-2 that possesses a 2-fold rotation symmetry, however, there are three sets of μ -OH and three sets of mixed μ -OH/HCO₂ linkers that interconnect the six [Zr₆] units. As a result, a 3-fold axis penetrates through the center of the hexameric wheel, at the intersection of three vertical planes of symmetry. Consequently, the whole molecule is closer to a undistorted circle with the diameter of 2.5–2.6 nm and is not bent compared to ZF-2. The BVS values of μ_2 -oxygen atoms in ZF-3 are in the range 1.00–1.16, also suggesting that they are all hydroxo groups. In ZF-3, three pairs of K⁺ and Cl⁻ ions are found for every [Zr₃₆] unit in the space between adjacent hexameric clusters (Figure 3b).

The subtle variations in the formula and geometry of the hexameric cycles of ZF-2 and -3 give rise to dramatic differences in packing structures. In ZF-3, a superstructure assembled from the hexagonal disc-like macromolecules is

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Figure 3. (a) Molecular structure of ZF-3 with its hexagonal shape emphasized by thick blue lines. (b) Intra- and intermolecular interactions involving K^+ (purple), Cl⁻ (organge), and formate groups. (c) $[Zr_{36}]_8$ supercage in the unit cell. Black dashed lines represent nonbonded contacts between adjacent $[Zr_{36}]$ macrocycles. The supercages of RHO (d) and pahasapaite (e) are shown for comparison.

immediately recognized. As depicted in Figure 3c, eight hexagonal cycles self-assemble into a hollow supercage with a tetrahedral symmetry. An imaginary sphere of 16 Å diameter would fit inside the cage without touching the van der Waals surface. The arrangement of the eight 6-rings in the supercage of ZF-3 resembles that of truncated cuboctahedron or the α cage of zeolite RHO (Figure 3d). In fact, the network structure of ZF-3 shown in Figure 4a is similar to a natural mineral of beryllium phosphate known as pahasapaite that has an array of distorted α cage of RHO (Figures 3e and 4b).¹⁵

The key interactions enabling the self-assembly in ZF-3 appear to be ion-dipole that involves K^+ and Cl^- ions and van der Waals contacts between formate ligands. As shown in Figure 3b, K^+ and Cl^- ions form nonbonded interactions with oxygen and hydrogen atoms, respectively, in both intra- and intermolecular fashion. The distance between K^+ and Cl^- is 3.131(6) Å and is very close to the ionic separation in KCl crystal (3.15 Å). The inclusion of KCl in the crystal structure explains why ZF-3 could be synthesized in a pure form only by adding KCl or KNO₃ to the reaction mixture.

When the oxygen-bound K^+ ions are considered as independent nodes connecting the edges between [Zr₆] nodes of adjacent 6-rings, the solid structure of ZF-3 may be simplified to a diagram shown in Figure 4c. We find out that the topology underlying this net is **pbp-e**, an edge net of **pbp** (Figure 4d).¹⁶ Note that **pbp** represents one of the two hypothetical 3-periodic nets predicted by O'Keeffe et al. as the simplest form of 3-coordinate carbon.¹⁷

The void fractions estimated from the single crystal data of ZF-2 and -3 are 44% and 47%, respectively.¹⁸ The measurable porosity of the two in the bulk solid forms, however, could be much lower than the expected values because of the lack of



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Figure 4. Network structures of (a) ZF-3 and (b) pahasapaite. (c) Topological presentation of the net of ZF-3 where blue hexagons and purple atoms represent $[Zr_{36}]$ cycles and K atoms, respectively. (d) **pbp-e** net showing the edge-connection through a secondary atom shown in red.

permanent linkers between the macrocycles. Unlike conventional network solids including MOFs, the removal of lattice solvents in molecular solids such as ZFs could readily disrupt the crystal packing. Therefore, the effects of desolvation on the solid structures of ZF-2 and -3 have been monitored by XRPD measurements (Figure 5).



Figure 5. XRPD patterns for ZF-2 (left) and -3 (right) after solventexchange, evacuation, and resolvation.

As shown in Figure 5, changes in characteristic diffractions of ZF-2 are evident even after a few minutes of vacuum treatments. Interestingly, the shift to higher 2θ values is most prominent for (111) reflections while (h00) and (0k0) reflections are not affected, meaning the shrinkage of intermolecular packing only along the *c* axis. This has also been confirmed by indexing the XRPD patterns after a complete evacuation (Figure S6). While the changes in *a* and *b*

dimensions are negligible (~0.1 Å), the *c* dimension has significantly shortened from 15.77 to 14.05 Å. In case of ZF-3 which has a cubic lattice, the shift of Bragg diffractions to higher 2θ has been observed in all directions (Figure 5). After a complete evacuation of ZF-3 at 100 °C for 12 h, the reduction in *d*-spacing for (002) reflections is from 19.2 to 17.0 Å. The structural shrinkage and partial amorphization in ZF-2 and -3 are not permanent, and they can be fully reversed when the evacuated solids are resolvated using organic solvents as shown in Figure 5. In other words, ZF-2 and -3 can be activated without permanent structural damages by solvent-exchange and mild heating under 100 °C. Heating ZFs above ~200 °C leads to a gradual loss of formate linkers, and a complete decomposition occurs above ~300 °C according to thermogravimetric analysis (Figures S3 and S4).

In view of the highly flexible packing structures of ZFs established by XRPD, it is not surprising that activated samples of ZF-2 and -3 show nonporous behavior in gas sorption analysis with N₂, H₂, and CO₂ (Figure S7). The presence of highly polar groups over the entire macrocyclic molecule, however, implies that small and highly polar molecules may strongly interact with the Zr cluster-based molecular solids. Indeed, both ZF-2 and -3 display fast uptakes of water vapor at low relative pressure range ($P/P_0 < 0.3$) at 298 K (Figure 6).



Figure 6. Water vapor sorption isotherms at 298 and 308 K. Inset is the low pressure region.

The uptake capacities for water vapor by ZF-2 and -3 are similar up to $P/P_0 \approx 0.5$ which is equivalent to the relative humidity (RH) of 50%. The behavior of the two solids under higher humidity conditions, however, shows a marked difference. While the adsorption isotherm for ZF-3 having a cage-like void structure starts to saturate slowly as P/P_0 approaches 1, similar to microporous materials, ZF-2 shows type II behavior characterized by unrestricted monolayermultilayer adsorption.¹⁹ The unlimited uptake of water at high RH is rather unusual because most porous solids including zeolites and MOFs display either type I or type IV water sorption isotherms.²⁰ We believe that this is because the macrocycles in ZF-2 are in effect separated from one another and thus can readily expand allowing, in principle, unlimited amount of water molecules in the intermolecular voids until dissolution of the solid occurs. The presence of many steps in the adsorption profile of ZF-2 over the whole pressure range as shown in Figure 6 also implies that the water sorption is accompanied by structural changes. The adsorption of water at 308 K is overall similar to the one at 298 K except that the

uptakes are slightly lower at 308 K under low RH (<50%) conditions. Under high humidity conditions (RH > 50%), this feature typical for physisorption is reversed, and ZFs show slightly higher uptakes at higher temperature. We suppose that this is because the intermolecular packing can readily expand at higher temperatures.

The sorption of water vapor by ZFs appears to be selective not only against the common gases mentioned above, but also against ethanol as shown in Figure S4. Apart from the weakly interacting gas molecules, two factors may be considered as the reasons for the observed selectivity. First, ethanol has a much larger kinetic diameter (4.5 Å) compared to water (2.6 Å) while the largest openings to the intermolecular voids in ZF-2 and -3 are approximately 4 Å in as-synthesized crystals. The second reason may be attributed to the alkyl group of ethanol which are not expected to perceive strong attractions to the polar groups of ZFs.

Our work on the previously unknown phases of zirconium formate as detailed above has some implications on MOF research. From the synthesis point of view, ZFs show that the ubiquitous $[Zr_6O_4(OH)_4]$ unit can be interconnected by short hydroxo or formate linkers. Although such cases are not unprecedented,²¹ the assembly into a novel hexameric cycle $([Zr_6] \times 6)$ and self-assembly into a $\{[Zr_6] \times 6\} \times 8$ supercage has not been known in literature. In an alternate perspective, the hexameric cycles of ZF-2 and -3 may be viewed as a dimer of $[Zr_6]$ trimers and a trimer of $[Zr_6]$ dimers, respectively. Therefore, we believe that there may be other such combinations synthetically accessible.

As molecule-based porous solids, the selective and reversible sorption characteristics of ZF-2 and -3 may be used to develop functional materials for atmospheric water capture.²² The polar surface and confined cage-like void in ZF-3 leads to high isosteric heat (Q_{st}) of water adsorption (64.9–63.7 kJ/mol for 0-20.0 wt % H₂O) (Figure S9), enabling facile uptake even at low RH. $Q_{\rm st}$ (H₂O) values for ZF-2 which has a simple molecular packing structure are lower than ZF-3 and quickly drops from 52.7 to 42.0 kJ/mol on going from 0 to 20 wt % H_2O . The zero-coverage Q_{st} values for ZFs are considerably lower than those for zeolites, for example, 4A (117 kJ/mol),² 13X (108 kJ/mol),²⁴ and MgY (141 kJ/mol),²⁴ but are comparable to well-known MOFs, such as MIL-125-NH₂ (55 kJ/mol),²⁵ CoCl₂BTDD (55 kJ/mol),^{20a} and MOF-801 (72 kJ/mol).²⁴ Unlike these zeolites and MOFs in which the uptake of water vapor saturates at high RH (>80%), ZF-2 has a unique feature that adsorption is unrestricted at RH > 80%. This kind of behavior of molecular solids may be advantageous for adsorption-based dehumidifying system intended for hot and humid climate. If that would be the case, then moderate $Q_{\rm st}$ (H₂O) would be desirable because very high adsorption enthalpies, such as those for zeolites, impose an energy penalty for regeneration processes. As a proof of concept for the working principle, we tested the uptake of water vapor by ZF-2 and -3 under dynamic flow conditions at 298 K using gravimetric method (Figure 7).

For this experiments, Ar gas carrying water vapor at RH \approx 80(5)% was passed over the sample that had been preheated to 100 °C to remove lattice solvent molecules. As shown in Figure 7, both ZF-2 and -3 not only captures water vapor from gaseous stream at 298 K, but can be regenerated at moderate temperature of 353 K without significantly losing the working capacities within the span of measurements (98% and 97% for ZF-2 and -3, respectively). In accordance with the results of



Figure 7. Changes in weight of ZF-2 and -3 during isothermal uptake of water vapor at 298 K and regeneration at 353 K. Blue and red arrows mark the gas change to H_2O/Ar (RH $\approx 80\%$) and dry N_2 , respectively. Dashed lines are temperature profiles showing the effect of adsorption heat.

static water sorption at RH > 50%, ZF-2 has been found to possess higher working capacity (12.0 wt % or 46 H₂O per [Zr₃₆]) than ZF-3 (6.45 wt % or 25 H₂O per [Zr₃₆]). In a comparative study using zeolites 4A, it was necessary to raise the temperature at least to 453 K in order to fully regenerate after water uptake (Figure S10).

To summarize, we have shown that Zr_6 -formate-based macrocycles and supercage can be synthesized by simple, straightforward, and highly effective methods. The reactions involving in situ generation of carboxylate ligands may be applied to organic systems other than amides, for example esters. The highly unique and unprecedented $[Zr_{36}]$ cluster molecules may be further functionalized or interconnected into networks through mixed-ligand approach or postsynthetic solution processes.²⁶ It has also been shown that the high heat of water adsorption for ZF-3 and unrestricted uptake at high RH for ZF-2 are consequences of features observed in molecular packing structures. The strong tendency of early transition metals to form various high nuclearity clusters promises more exciting developments in porous molecular solids.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b06757.

Crystal data (CIF) Crystal data (CIF) Synthetic details, physical methods, crystal data, and Figures S1–S10 (PDF)

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Notes

The authors declare no competing financial interest.

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