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Nonporous Titanium–Oxo Molecular Clusters That Reversibly and Selectively Adsorb Carbon Dioxide

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Supporting Information

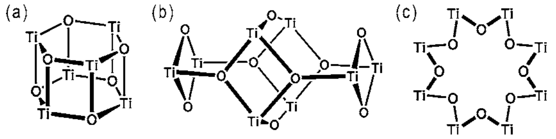
ABSTRACT: Nonporous titanium(IV) clusters supported by carboxylate ligands show selective sorption of carbon dioxide even in the amorphous phase. A ring-type Ti_8 cluster with a permanent inner pore also adsorbs gases, but not selectively.

One discerns molecular solids and materials based on molecular building blocks because the former implies the absence of intermolecular covalent or coordination bonds that form an extended network structure. The latter may include such new materials as metal–organic frameworks (MOFs; or coordination polymers) or covalent organic frameworks. The high interest in the molecule-based frameworks owing to their porous nature has recently inspired the study of molecular solids, and therefore many existing or new molecular materials that possess a permanent porosity exemplified by reversible gas sorption have been discovered and reported.[1]

The porous molecular solids may have intrinsically developed inner pores or intermolecular voids in the crystal lattice. Regardless of the structure types, most of the recent studies in this area have focused on organic systems,[2] and inorganic molecules showing reversible sorption properties are very rare.[3] This is rather surprising because rich variations in the structures of polynuclear metal–organic clusters should provide good opportunities to discover porous molecular solids.[4] Metal–oxo clusters, for example, often form hollow ring-type structures with alkoxo and/or carboxylate ligands.[5] However, the possibility of using these metal–oxo clusters as potential molecular adsorbents has almost completely been overlooked.

This led us to systematic investigations on the synthesis and gas-sorption properties of multinuclear metal–oxo carboxylate compounds. Our first target was the titanium(IV)-based octanuclear ring-type cluster that has been observed as a discrete molecule[6] or as the secondary building unit (SBU) of a hydrothermally stable MOF.[7] While attempting to reproduce the Ti_8 ring structure with 4-aminobenzoate, we discovered that two different products are obtained depending on the reaction conditions. Hereby we report the X-ray crystal structures of the new titanium(IV)–oxo carboxylate clusters and compare their gas-sorption properties with those of a related compound whose porous behavior has not been reported (Scheme 1).

Scheme 1. Geometry of the Titanium(IV)–Oxo Core Units of Compounds Studied in This Work



Titanium(IV) isopropoxide reacts with an excess amount of 4-aminobenzoic acid (Habz) under solvothermal conditions to form two kinds of crystalline solids depending on the solvents. In 2-propanol, yellow rod or octahedral crystals form, while in benzonitrile, orange-red thin-plate crystals are obtained. We observed no other crystalline phase by using different sources of titanium(IV) or other solvents including toluene, acetonitrile, ethanol, and *N*,*N*-dimethylformamide (DMF).

The optimized synthesis does not require the use of extra-dry solvents or an inert atmosphere and is highly reproducible. The products are somewhat soluble in DMF and do not dissolve in acetonitrile, chloroform, dimethyl sulfoxide, tetrahydrofuran, toluene, and water. In thermogravimetric analysis, no decomposition is observed before 260–280 °C in air for both compounds (Figures S1 and S2 in the Supporting Information, SI).

The identities of the two products were elucidated by X-ray crystallographic analysis on very small single crystals using synchrotron radiation (Figure 1).

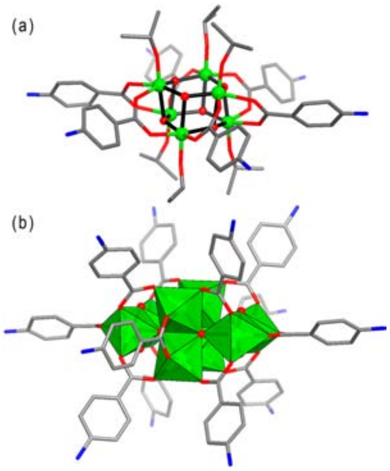


Figure 1. Molecular structures of **1** (a) and **2** (b). H atoms are omitted for clarity. Color: green, Ti; red, O; blue, N, gray, C.

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The yellow product is a Ti_6 cluster with the formula $[Ti_6O_6(abz)_6(O^iPr)_6](^iPrOH)_n$ ($\mathbf{1}\cdot{}^iPrOH$), and the two different habits mentioned above (rod and octahedral) correspond to triclinic ($P\bar{1}$) and cubic ($Pa\bar{3}$) phases, respectively. They are different only in the amounts of crystallization solvents because of the differences in molecular packing.[8] The orange-red product obtained from benzonitrile is formulated as $[Ti_8O_{10}(abz)_{12}](PhCN)_{3.6}$ ($\mathbf{2}\cdot PhCN$).

The bulk purity of the products is supported by elemental analysis and Fourier transform infrared spectra, which show an exact match from one batch to another (Figure S3 in the SI). Powder X-ray diffraction (PXRD) provides conclusive evidence for the purity of the crystalline phase for **1**. For **2**, only diffraction for (100) is observed at the expected 2θ position (Figure 2).

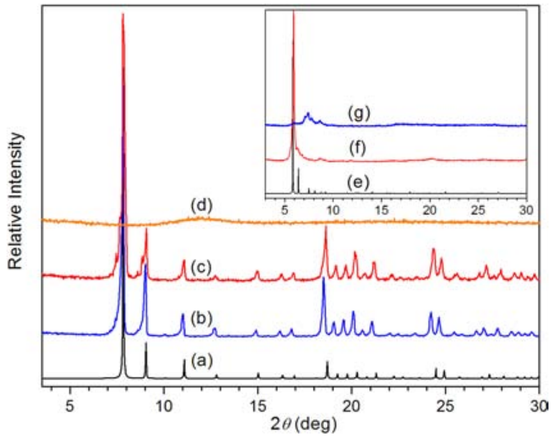

Figure 2. PXRD patterns of **1**: (a) simulated; (b) as-synthesized; (c) evacuated; (d) after water treatment. The inset shows PXRD patterns for **2**: (e) simulated; (f) as-synthesized; (g) evacuated.

In the molecular structure of **1**, the Ti_6O_6 core adopts a hexagonal column geometry and is supported by six abz ligands on the equatorial plane (Figure 1a). The octahedral coordination sphere of each Ti^{4+} is completed by an isopropoxide anion along the vertical direction. The bond distances and other geometrical features of **1** closely resemble those of previously reported Ti_6 clusters with other carboxylate ligands.[9]

The structure of **2** consists of eight Ti^{4+} ions bridged by six μ_2-O and four μ_3-O atoms (Scheme 1b), and overall the cluster is supported by 12 carboxylate ligands (Figure 1b). In an alternate description, four pairs of edge-sharing TiO_6 octahedra are joined to each other in a corner-sharing fashion. To the best of our knowledge, the octanuclear cluster found in **2** has never been documented for Ti or other metal ions.[10]

The crystal packing of **1** in the cubic phase is not governed by a specific secondary interaction and forms an ABCABC... type close packing along the [111] direction. Small isolated pores of 5 Å width are found in the places equivalent to octahedral sites in a cubic close packing (Figure S7 in the SI). The solvent-accessible void in the structure of **1** is about 10% of the total crystal volume.

The molecular packing of **2** is somewhat less efficient than that of **1** and can be best described as a layered packing with a rhombic grid-type pattern on (100) planes (Figure S8 in the SI). Adjacent layers are weakly held by $\pi-\pi$ interactions between abz ligands and leave a large portion of the solvent-occupied volume in interlayer spaces (~33%). Disordered benzonitrile molecules occupying the void have been structurally characterized.

The different molecular packings of **1** and **2** result in contrasting behavior of the bulk solids, as shown by PXRD measured after removal of the included solvent molecules. The densely packed structure of **1** is well-maintained even after the as-synthesized material is heated to 100−200 °C for 12 h under vacuum (Figure 2c), while **2** loses the long-range order and bulk crystallinity upon complete desolvation (Figure 2g).

The rigidity of densely packed solid **1** and the lack of crystallinity in evacuated solid **2** are not desired attributes for a porous solid in general. Indeed, the activated samples of **1** and **2** do not display a meaningful amount of nitrogen sorption up to 1 bar. At 195 K, however, not only do both **1** and **2** show a significant uptake of carbon dioxide, but the sorption is selective against nitrogen and methane (Figure 3).[11]

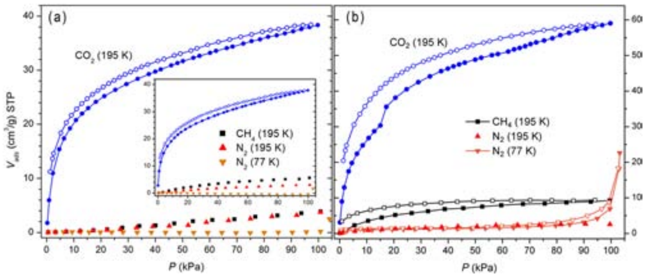

Figure 3. Gas-sorption isotherms measured for **1** (a) and **2** (b). Inset of part a: results from a water-treated sample of **1**. Filled and open symbols denote adsorption and desorption, respectively.

The stepped adsorption and pronounced hysteresis observed for **2** are believed to originate from the inefficient molecular packing, as described above.

The selective and reversible adsorption of carbon dioxide by molecular titanium clusters without inner pores occurs exclusively through intermolecular voids and is irrelevant to ordered packing structures. We provide two strong evidences for this claim. First, the well-maintained crystal packing of evacuated **1** is completely disrupted when the material is stirred in water for several hours (Figure 2d). The water-treated, amorphous solid of **1**, however, gives the same results in the gas-sorption experiments (Figure 3a). Second, we reproduced and measured the gas sorption for a ring-type Ti_8 cluster without the $-NH_2$ group in the benzoate ligand, $[Ti_8O_8(benzoate)_{16}]$ (**3**; Figure 4).[6] The hollow molecule shows an interesting two-step adsorption for carbon dioxide at 195 K. At pressures below $P/P_0 \sim 0.6$, a perfectly reversible type I adsorption is observed because of the permanent intramolecular pore. The almost saturated adsorption then shows a sudden increase with large hysteresis at higher pressures. Similar to the cases of **1** and **2**, this latter uptake is due to the lattice voids that interconnect between adjacent ring molecules. Also noted from Figure 4b is the absence of selective sorption against nitrogen and methane at 195 K. Again, this is due to the presence of a permanent inner pore in **3**, unlike the case of **1** or **2**.

The results of our gas-sorption experiments may be summarized as follows. A nonporous molecular cluster with rigid side groups may exhibit reversible and selective sorptions for carbon dioxide, which has a small kinetic diameter (3.3 Å) and a strong quadrupole moment interacting with polar regions of the surface.[12] This is because even in the amorphous phase intermolecular voids are available due to the rigid molecular geometry. A ring-type cluster with a permanent inner pore and

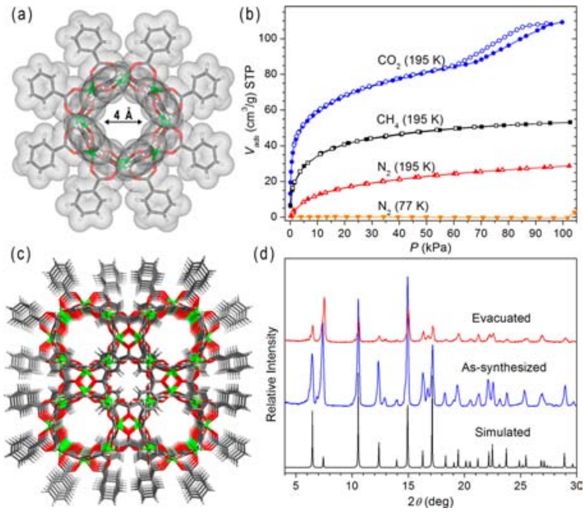

Figure 4. Molecular (a) and packing (c) structures of **3** and its gas-sorption (b) and PXRD (d) patterns.

rigid side groups shows higher uptake of gases but at the cost of selective sorption capability.

Molecular metal−oxo clusters possess clear advantages over MOFs as potential adsorbents. First, unlike most MOFs, these molecular materials do not lose sorption properties upon amorphization and therefore can be applied in a wide range of situations including humid air. Second, being inherently discrete in nature, these materials are soluble and therefore can readily be modified or processed into other forms using solid or solution techniques.[13] Finally, the facile synthesis and vast structural diversities of metal−oxo clusters are nearly comparable to those of MOFs and are not paralleled by organic cage molecules. Considering the strong tendency of early transition metals, such as titanium(IV), vanadium(IV/V), and their heavier congeners, to form oxo-bridged multinuclear clusters, the prospect of discovering new molecular solids with even more interesting properties should be very high. We hope that the results of this work will renew interest in this exciting class of materials.

In conclusion, we showed two examples of nonporous titanium(IV)−oxo carboxylate clusters that reversibly and selectively adsorb carbon dioxide even in the amorphous phase. The results that we obtained hint at the possibilities of discovering many new molecular adsorbents from conventional metal cluster chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, details of the synthesis and characterization, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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