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$Na_2Zn_3(CO_3)_4{\cdot}3H_2O$, a Microporous Sodium Zincocarbonate with a Diamond-Type Tetrahedral-Triangular Topology

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Microporous open frameworks, built from corner sharing of tetrahedra of suitable metal(oid) atoms and oxygen atoms, are well-known. Zeolites (aluminosilicates) are produced synthetically in ton quantities annually for a variety of commercially important uses. In the 1980's, open frameworks based on aluminum and phosphorus tetrahedra (AlPO's)[1] were discovered, many with structures analogous to some of the zeolites despite the fact that the frameworks were neutral instead of negatively charged. More recently, a wide variety of microporous structures based on zinc, beryllium, phosphorus, and arsenic tetrahedra have been demonstrated.[2,3]

We have been interested for some time in the synthesis and crystal growth of new open framework structures containing novel metal(oid) atoms, ligands, or coordination numbers. In oxide based materials, the most common coordination encountered is tetrahedral and the framework metal(oid) atoms are referred to as "T" atoms. In the last few years novel materials with Ga in 5 coordination[4] and Al[5] and Mn[6] in 6 coordination have been synthesized. Tetrahedral ZnO_4 and triangular planar BO_3 exist in $Zn_4O(BO_3)_2$[7] and $MZn_4(BO_3)_3$[8] (M = K, Rb, Cs), but the two building blocks do not alternate regularly. We have explored the possibility of forming frameworks containing planar triangular building blocks (carbonate, borate, or nitrate) in combination with tetrahedral centers to see if such structures might possess interesting features. Zinc carbonates typify an area of our recent research. Aside from the minerals smithsonite, $ZnCO_3$,[9] and hydrozincite, $Zn_5(CO_3)_2(OH)_6$,[10] little is known of these materials or their alkali metal derivatives. $Na_2Zn_3(CO_3)_4{\cdot}3H_2O$[11] and $Na_6Zn_8(CO_3)_{11}{\cdot}8H_2O$[12] have been reported with identical powder diffraction patterns. Here we report on the synthesis, crystal growth, and single crystal structure of $Na_2Zn_3(CO_3)_4{\cdot}3H_2O$.

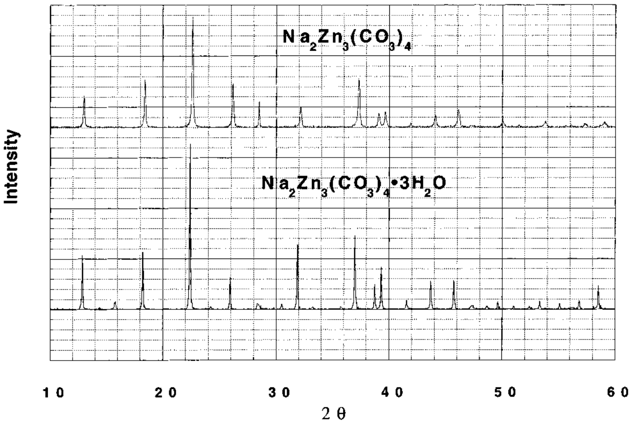

Figure 1. Powder diffraction pattern of hydrated and dehydrated samples. The pattern changes from primitive cubic to face-centered upon dehydration at 190 °C. The peak positions shift slightly toward the high angle for the dehydrated sample indicating the contraction of the cell.

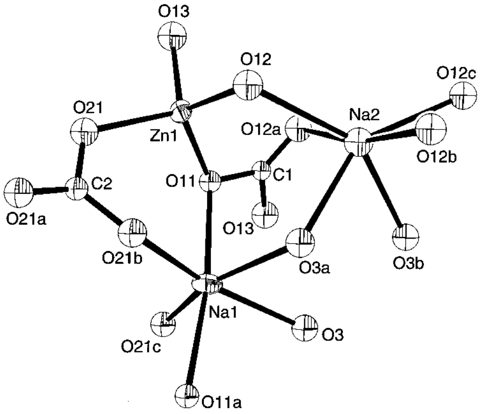

Figure 2. Local polyhedral environments for zinc, carbon, and sodium cations. The O3 belongs to the extra-framework water molecule. The Na2 is shown at one of two statistical positions. Atom labels having "a", "b", and "c" refer to symmetry generated atoms. Only Zn1 and Na1 are refined anisotropically.

$Na_2Zn_3(CO_3)_4{\cdot}3H_2O$ is prepared as a microcrystalline powder by adding slowly 12.60 g of $NaHCO_3$ to 60 mL of 0.8 M $ZnCl_2$. Carbon dioxide evolves rapidly and a white precipitate forms. After holding for 5 h at 70 °C, the settled white solids are filtered off to yield 8.2 g of product. The powder diffraction pattern can be indexed cleanly as primitive cubic (Figure 1), a = 13.741(1) Å. Thermogravimetric analysis reveals 10.4% weight loss at 190 °C which agrees with the calculated value of 10.1% for $3H_2O$. The cubic structure is stable to water loss; however, the powder diffraction pattern changes from primitive to face-centered cubic upon dehydration (Figure 1) and the cell volume contracts by about 2.2%. The structure can be reversibly dehydrated. At higher temperatures, CO_2 is lost to leave a residue of ZnO and Na_2CO_3.

Small sparkling tetrahedra of the sodium zinc carbonate hydrate can be grown by sealing 0.67 g of the above powder in a gold tube, along with 0.84 g of $NaHCO_3$ and 0.5 mL of H_2O. The tube is inserted in a Tem-pres (LECO) hydrothermal apparatus and heated to about 550 °C under a support pressure of 30 000 psi for 10 h. Subsequently, it is cooled at 6 °C/h to 300 °C and then furnace cooled to ambient conditions. The product, following a hot water wash to remove excess $NaHCO_3$ mineralizer, is several clear tetrahedra up to 0.25 mm on an edge. The crystals are air and moisture stable, but dissolve in dilute acid.

The asymmetric unit is $Na_{1/2}Na_{1/6}(H_2O)[Zn(CO_3)(CO_3)_{1/3}]$ with two crystallographically different carbon and sodium atom sites (Figure 2). The strictly alternating ZnO_4 tetrahedra and CO_3 triangles share all corners. The ratio of tetrahedral atoms (Zn) to triangular atoms (C) is in the ratio of the connectivity

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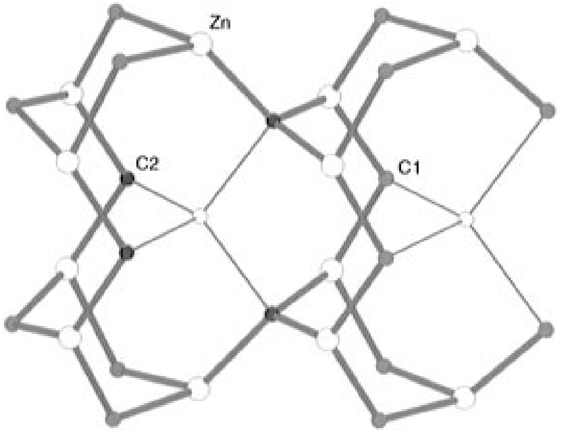

Figure 3. The two types of unoccupied tetrahedral sites in the diamond-type framework lead to the interruption of admantane cages and boat-shaped eight-rings. The vacant sites are drawn as two smaller open circles. Two labeled carbon atoms are in the eight-rings shown here.

of C to the connectivity of Zn, i.e. 3/4. This holds true for other completely corner sharing tetrahedral−tetrahedral or tetrahedral−octahedral frameworks such as $Zn_3(Fe(CN)_6)_2$ in which the ratio of tetrahedral to octahedral sites is 6/4. Na2 atoms are located on a 2-fold axis with a chemical occupancy of 1/3. Its content in the asymmetric unit, 1/6, is computed from the crystallographic occupancy (1/2) and its chemical occupancy. Since the Na2 site is less than 1.0 Å away from a 4-fold inversion axis, Na2 atoms are statistically distributed on two sides of the symmetry axis. The other extra-framework species, Na1 cations and water molecules, are fully ordered.

The framework structure is closely related to the diamond-type structure. The tetrahedral zinc and triangular carbon atoms form a diamond-type network. Compared to the diamond structure, one-eighth of the tetrahedral sites are vacant due to the triangular connectivity of the carbonate carbon atoms. There are two crystallographically distinct vacant sites (Figure 3). One is at the center of the tetrahedra formed by four C1 atoms and is located at the cubic cell origins and the body center. The other type of vacant site is at the center of the tetrahedra formed by four C2 atoms and is located at the cubic face and edge centers. These vacant T-sites form the center of novel cages consisting of six eight-rings facing {100} directions and four six-rings facing {111} directions. Each cage has 12 tetrahedral atoms and 16 triangular atoms.

There are a total of eight vacant tetrahedral sites per cell, which leads to the loss of 56 out of 64 possible admantane cages per cell. The eight remaining admantane cages are centered on the cubic body diagonals at {1/4 1/4 1/4}. The three-dimensional framework can be viewed as a network of corner-sharing admantane cages with the simple cubic packing mode (Figure 4). Each admantane cage has six zinc and four carbon atoms. The six zinc atoms are distributed similar to six corners of an octahedron. The 3:4 ratio between zinc and carbon atoms is obtained because each zincate tetrahedron is shared between two adjacent cages just like corner-sharing octahedra.

As expected from the diamond-type structure which contains only six-rings, the smallest ring size in the structure is six, consisting of three tetrahedral zinc and three triangular carbon atoms. There are two types of geometrically similar eight-rings in the equal ratio, consisting of 2 × (Zn-C1-Zn-C2) (Type I) and 4 × (Zn-C1) (Type II), respectively. The framework has three-dimensional orthogonal channels along the cubic cell axes with boat-shaped 8-ring openings. Sodium ions and extra-framework water molecules are located in the channels near the eight-ring openings. Each "Type I" eight-ring has a Na1 atom anchored there while only a third of the "Type II" eight-rings have Na2 atoms nearby. The distorted Na1 octahedron consists of four framework oxygen atoms and two crystallographically identical water molecules cis to each other. Na2 is also coordinated to four framework oxygen atoms, but with two pairs of water molecules nearby. As a result, Na2 has the option of coordinating to either pair and is thus statistically distributed at two possible positions.

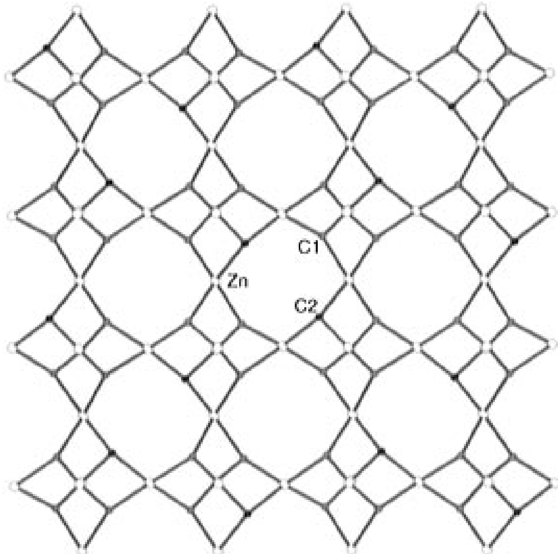

Figure 4. The tetrahedral−triangular atom connectivity diagram viewed down the eight-ring channels in the crystallographic {100} direction. The two types of eight-rings consist of 2 × (Zn-C1-Zn-C2) and 4 × (Zn-C1), respectively. The framework is built from corner-sharing admantane cages.

The pore sizes for "Type I" and "Type II" eight-rings are 1.8 × 1.4 and 2.1 × 2.1 Å, respectively, based on the oxygen van der Waals radius of 1.35 Å. They are small due to the short C−O bond and significant non-coplanarity of the eight-rings. This explains why the considerably higher temperature of 190 °C is required for the removal of water molecules.

One important feature of the structure is its pseudo-symmetry. Especially, the two heaviest elements, Zn1 and Na1 belong to the supergroups, $F\bar{4}3c$ and $I\bar{4}3m$, respectively, which result in all reflections containing an odd *h*,*k*,*l* indice systematically weak.

The tetrahedral−triangular framework can be compared to some interrupted tetrahedral−tetrahedral frameworks. CO_3^{2-} is similar to $PO_3(OH)^{2-}$ which has been found in some interrupted zincophosphate structures. Both groups have a negative charge of −2 and have three bridging groups. However, dangling hydroxyl groups in phosphates often block pore openings. Since interrupted frameworks such as cloverite generally have lower T-atom density and larger ring-sizes, it might be expected that tetrahedral−triangular frameworks could give rise to a similarly low-density, large-ring size framework and thus be potentially useful in the design of large-pore open frameworks. We have in fact recently synthesized an interrupted framework structure with only 12-ring pore openings and a T-atom density less than that of cloverite.

Single crystal data for $Na_2Zn_3(CO_3)_4 \cdot 3H_2O$ (or written as $\{(Na_{3/2})(Na_{1/2})(3H_2O)\}\{(ZnO_2)_3(CO_{1.5})_3(CO_{1.5})\}$): cubic, $P\bar{4}3n$ (No. 218), $a = 13.7549(3)$ Å, $V = 2602.4(2)$ Å^3, $Z = 8$, $D_c = 2.74$ g cm^{-3}, clear tetrahedron, Mo Kα, $\lambda = 0.71073$ Å, $\mu = 5.78$ mm^{-1}, R = 6.89%, $wR = 7.69\%$, GOF = 1.34 for 45 parameters and 587 unique reflections with $I > 3.0\sigma(I)$.

Supporting Information Available: X-ray crystallography data including tables of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (8 pages); listing of structure factor amplitudes (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current meastheads page for ordering information and Internet access instructions.

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