Inorg. Chem. **2006**, *45*, 10410–10412

Inorganic Chemistry

Communication

Sodium Zinc Hydroxide Sulfite with a Novel Zn_3OH Geometry

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Received September 4, 2006

The synthesis and crystal structure of a new sodium zinc hydroxide sulfite, $Na[(Zn(OH)]_3(SO_3)_2$, with novel structural features and bonding geometry are reported. In $Na[(Zn(OH)]_3(SO_3)_2$, Zn^{2+} and O^{2-} alternate to form an interesting corrugated hexagonal sheet with rings consisting of $(ZnO)_3$. Another rare occurrence is the bonding geometry of one-third of the O sites within the sheet. These O sites form a planar Zn_3O unit, unlike other known compounds, in which Zn_3O is pyramidal.

Even though open-framework and microporous solids have been made in a variety of different compositions such as silicates, phosphates, germanates, borates, and phosphites, few are known that are based on trigonal-pyramidal sulfite anions (SO_3^{2-}). Our interest in the zinc sulfite composition stems from the desire to probe the bonding characteristics of SO_3^{2-} units particularly in comparison with other building blocks and to create framework materials from 3- and 4-connected units.[1,2]

Here we report a new sodium zinc hydroxide sulfite with unusual structural features. In this compound, one-third of the O sites form a perfect planar Zn_3O group. To our knowledge, such an O-bonding geometry in the Zn_3O group is extraordinary because previously reported Zn_3O (or Co_3O) units always adopt pyramidal geometry.[3−5]

The title compound was prepared by hydrothermal synthesis.[6] The crystal structure was determined by low-temperature, high-resolution single-crystal data (0.50 Å and $2\theta_{max} = 90°$) collected at 150 K.[7] All atoms including H atoms were located experimentally from Fourier or difference Fourier maps. In $Na[(Zn(OH)]_3(SO_3)_2$, Zn^{2+} and OH^- alternate to form an interesting corrugated hexagonal sheet with six-membered rings consisting of $Zn_3(OH)_3$ (Figure 1). Such a hexagonal sheet is quite uncommon because six-membered rings commonly encountered (particularly in open-framework silicates and phosphates) are $(Al-O-Si)_3$ type rings that contain six cationic centers (usually tetrahedral atoms) rather than three centers as reported here.[8]

The SO_3^{2-} group is bonded to the Zn−O layer from both sides of the layer in the tripod fashion (Figure 2). Each Zn^{2+} site serves as the common foot of two SO_3^{2-} groups from two opposite sides. As a result, the Zn^{2+} site adopts the trigonal-bipyramidal geometry with three equatorial O sites [Zn−O = 2.013 and 2.024 Å (2×)] within the sheet and two axial O sites [Zn−O = 2.096 Å (2×)] from two separate SO_3^{2-} groups.

The sheet is perpendicular to the hexagonal *c* axis, with the interplanar distance equal to half of the periodicity along the *c* direction (6.654 Å). Two adjacent layers are joined together through octahedrally bonded Na^+ sites (Na−O = 2.444 Å). Each Na site is bonded to one O atom on each SO_3^{2-} group (Figure 3).

Within the hexagonal layer, there are two crystallographically unique O sites (O1 and O2), with the O2 site twice as abundant as the O1 site (Figures 1 and 2). When viewed along the direction perpendicular to the Zn−O layer (the *c* direction), the O2 site is located exactly below the SO_3^{2-} group. Therefore, the proton on the O2 points away from the layer on the opposite side of the SO_3^{2-} group. This leads to the familiar tetrahedral geometry for O2 in the Zn_3OH

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(6) In a typical synthesis, a total of 0.1236 g of zinc carbonate, 0.2583 g of sodium sulfite, and 5.288 g of water were mixed in a 23-mL Teflon-lined stainless steel autoclave and stirred for 30 min. The pH of the resulting mixture was adjusted to 6.79 using 0.2429 g of 1,4-bis(3-aminopropyl)piperazine and 0.254 g of acetic acid. The vessel was sealed and heated at 120 °C for 7 days. After cooling to room temperature, clear hexagonal-prism-shaped crystals were obtained with a 32.8% yield.

(7) Crystallographic data for $Na[(Zn(OH)]_3(SO_3)_2$, space group $P\bar{3}c1$ (No. 165), $0.18 \times 0.18 \times 0.20$ mm^3, $a = 5.8494(1)$ Å, $c = 13.3086(2)$ Å, $V = 394.35(1)$ Å^3, $Z = 2$, Mo Kα, $T = 150$ K, $2\theta_{max} = 90°$, $R(F) = 1.89\%$ for 29 parameters and 1094 reflections with $I > 2\sigma(I)$.

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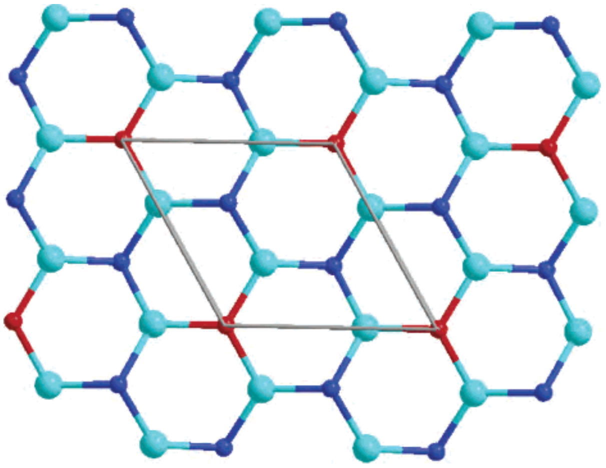

Figure 1. Corrugated hexagonal sheet built from alternating Zn^{2+} (large circles in cyan) and hydroxyl O (red, O1; blue, O2) sites.

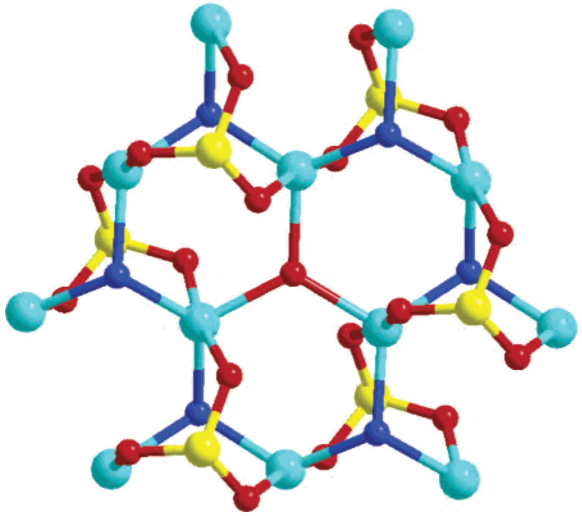

Figure 2. Tripod-type bonding between SO$_3^{2-}$ and a Zn$-$OH hexagonal sheet. Three SO$_3^{2-}$ groups (six total) are shown on each side of the sheet. Color code: cyan, Zn; yellow, S; blue, O2; red, O1 or O3 (sulfite O).

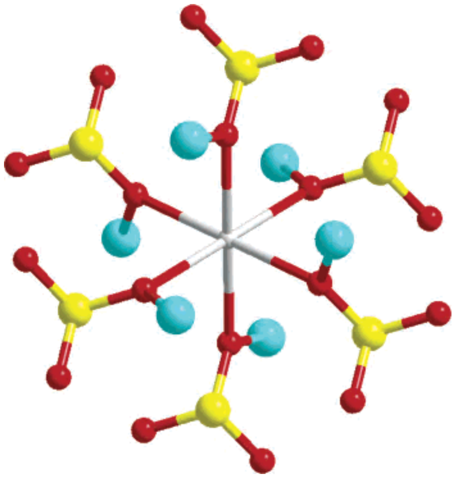

Figure 3. Primary coordination environment of the Na^{+} site. Color code: cyan, Zn; yellow, S; red, O3; gray, Na.

unit. Tetrahedrally coordinated O sites, in the form of M$_3$(OH)$^{5+}$, are very common and have been found in hundreds of Zn and Co compounds.[3−5]

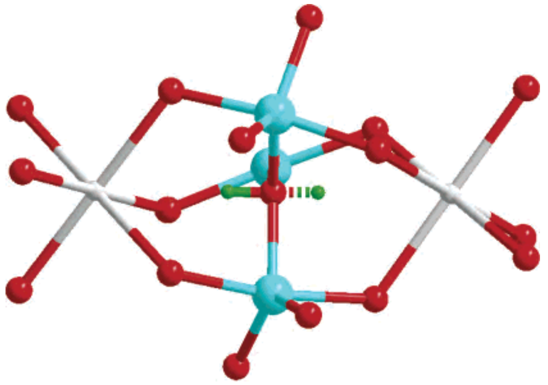

Figure 4. Two NaO$_6$ octahedral surrounding the interesting Zn$_3$OH unit. Color code: cyan, Zn; red, O; gray, Na; green, H.

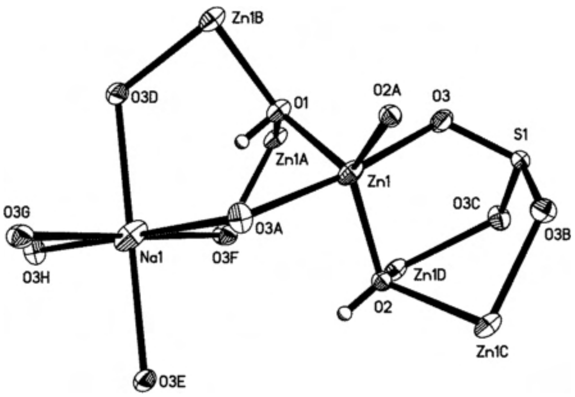

Figure 5. ORTEP drawing at the 50% probability level of the local bonding environments of atoms in the asymmetric unit. Atom labels containing “A”, “B”, or “C” indicate symmetry-generated sites.

On the other hand, the two sides of the O1 site are open (i.e., not occupied by SO$_3^{2-}$ groups) as shown at the center of Figures 2 and 4. The O1 coordination to three Zn^{2+} sites is strictly triangular-planar (Zn$-$O$-$Zn $=$ 120°). The proton is therefore statistically distributed on two sides of the O1 site. It is worth commenting that O and Zn sites are not disordered (Figure 5) and the above interesting geometry is not caused by structural or thermal disorder of O or Zn sites. In addition, to ensure the reliability of the X-ray refinement results, data collection was performed at 150 K to a maximum 2θ of 90° (0.50 Å).

The placement of a proton on the O1 atom is also supported by the bond valence calculation.[9] The bond valence sum from the O1 atom to its adjacent Zn^{2+} sites is only 1.26, which suggests that the O1 atom is underbonded in the absence of a proton and that it should be a hydroxyl group, similar to the O2 site. The only other O site, the O3 atom within the SO$_3^{2-}$ group, has a bond valence sum of 1.87 (0.347 for Zn$-$O, 1.35 for S$-$O, and 0.177 for Na$-$O) and is much less likely to accept a proton than the O1 atom with a bond valence sum of only 1.26.

There are many examples of Zn$_3$OH (or Co$_3$OH) units and, to our knowledge, all of them adopt tetrahedral geometry (with various degrees of distortion) with the pyramidal Zn$_3$O unit.[3−5] It is therefore interesting to investigate the cause for the unusual planar Zn$_3$(OH) geometry reported here. It is

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(9) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

suggested here that the electrostatic repulsion between Na^+ and H^+ along the O−H direction is responsible for forcing the otherwise pyramidal Zn_3O unit into a perfectly planar configuration. In this compound, Na^+, O1, and a proton on O1 form a strictly linear chain (Figure 4). Because there is one Na^+ site at both sides of the hydroxyl group, the conventional tetrahedral Zn_3OH geoemtry would bring H^+ too close to the Na^+ site to be stable. The formation of the planar Zn_3O unit as reported here may serve the purpose for the maximum separation between Na^+ and H^+ (Na···H = 2.45 Å and O−H = 0.87 Å in this case).[10] It is worth noting that each Na site is already fully coordinated to six O atoms from six SO_3^{2-} groups (Figure 3). The Na···H contact discussed here is between the Na site and the hydroxyl group of the $Zn_3(OH)$ group, and there is no bond between any Na^+ site and the hydroxyl O atom (O1). As shown in Figure 4, the suggested Na···H interaction does not interfere with the regular Na−O bonding.

Acknowledgment. We are thankful for support of this work by NIH (Grant 2 S06 GM063119-05), Research Corp. (Grant CC6593), and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 41382-GB10). We thank Dr. Lei Han for his help with the initial crystallographic work.

Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The X-ray-derived bond distances involving H sites are less accurate because of the asymmetric distribution of the electron density around the H nucleus.