

# Novel lamella hydrated sodium zinc arsenate with 4-connected two-dimensional nets

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Hydrothermal synthesis and crystal structure of a lamellar hydrated sodium zinc arsenate with an unusual sheet structure are reported.

Metal phosphates and arsenates are of interest for their chemical and physical properties and resulting applications as catalysts, non-linear optical materials, ion-exchangers *etc.*<sup>1</sup> Since the 1980s, many phosphate based zeolite analogs and novel structures have been synthesized.<sup>2</sup> This has further expanded the possible applications of metal phosphate based materials. Divalent metal phosphates and arsenates have the same total charge (+2 and +5) as that of zeolite aluminosilicates (+3 and +4). This has generated a lot of interest in synthesizing zeolite structural analogs in the T<sup>2+</sup>/T<sup>5+</sup> system (T refers to a tetrahedral atom).<sup>3</sup> A number of zeolite structural analogs have been synthesized, including Na<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub>(ZnPO<sub>4</sub>)<sub>6</sub> (sodalite), (Na, TMA)<sub>96</sub>M<sub>96</sub>P<sub>96</sub>O<sub>192</sub> (M = Be, Zn; zeolite X), Li<sub>4</sub>M<sub>4</sub>-P<sub>4</sub>O<sub>16</sub>·4H<sub>2</sub>O (M = Be, Zn; zeolite Li-ABW) and Li<sub>24</sub>Be<sub>24</sub>-P<sub>24</sub>O<sub>96</sub>·4H<sub>2</sub>O (zeolite RHO).<sup>4</sup> Very recently, a large family of cobalt phosphate based zeolite structural analogs have been reported.<sup>5,6</sup>

The framework of a zeolite structure has the general composition of AB<sub>2</sub>, where A is a 4-connected atom (tetrahedral atoms such as Al, Si, Zn, Be, P, As . . .) and B is any 2-connected atom (usually oxygen) which is shared between two tetrahedral atoms. The topology of zeolite structures is usually viewed based on the connectivity of tetrahedral atoms. Such a tetrahedral atom connectivity can be regarded mathematically as 4-connected 3D nets, which are constructed from 3-connected 2D sheets.<sup>7</sup> Thus, both 4-connected 3D nets and 3-connected 2D sheets are common among known structures. To our knowledge, however, there is no reported example of a structure in which tetrahedral atoms form 4-connected 2D sheets. In known structures, when lamellar structures are formed from tetrahedral atoms, there are always interruptions involved and the resulting structures, even if polymeric, are not completely 4-connected.<sup>8</sup>

Here, we report an unprecedented occurrence of 4-connected 2D sheets in a new hydrated sodium zinc arsenate. Owing to the formation of 4-connected sheets, no pendant oxygen atoms, hydroxyl groups or water molecules are present on the anionic sheet. Such a novel sheet structure could lead to interesting properties such as the ion-exchange characteristics.

The title compound was synthesized under hydrothermal conditions typically used in the synthesis of zeolites. To a polypropylene bottle was added 9.36 g of Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O (30 mmol), 0.8 g of NaOH pellets (20 mmol) and 25 ml of water. To the clear solution was then added 12.0 ml of a 2 M solution of Zn(NO<sub>3</sub>)<sub>2</sub> (24 mmol) and the resulting gel was shaken thoroughly to give a thick white slurry. The slurry settled rapidly (pH = 6.5) and after standing overnight at 50 °C was recovered by standard filtration and drying techniques. Small crystals (6.282 g) were obtained at 99.4% yield. Thermal analysis showed that the material had a mass loss of 13.2% up to 210 °C with no further loss to 500 °C (calc. 13.7% for NaZnAsO<sub>4</sub>·2H<sub>2</sub>O). The residue at 500 °C was identical to the hexagonal product from the calcination of Na<sub>6</sub>(ZnAsO<sub>4</sub>)<sub>6</sub>·6H<sub>2</sub>O (sodalite structure).<sup>9</sup>

The pH and temperature are critical to the formation of this phase. At higher pH, the sodalite phase appears and at lower pH an unidentified material appears. Even at pH = 6.5, heating to 100 °C for any period of time converts the title compound to the latter unidentified phase.

The crystal structure was solved using data collected on a Siemens SMART CDD diffractometer.† A full sphere of intensity data were collected with  $\omega$  scans (width of 0.30 and exposure time of 30 s per frame). Final full-matrix refinements were against  $F^2$  with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were not included.

The asymmetric unit is NaZnAsO<sub>4</sub>·2H<sub>2</sub>O with two unique sodium cations located at inversion centers. Tetrahedral atoms (Zn and As) are connected by oxygen atoms to form an infinite sheet (Fig. 1). Like zeolite structures, there is a strict alternation of ZnO<sub>4</sub> and AsO<sub>4</sub> tetrahedra which explains the Zn/As ratio of unity. The unique feature of the title arsenate is that all corners of Zn and As tetrahedra are shared with adjacent tetrahedra. This is unprecedented for a lamellar structure constructed from tetrahedral centers. The resulting sheet can thus be described as a 4-connected 2D net.

Both two unique sodium cations are octahedrally coordinated. Each sodium cation is coordinated to two oxygen atoms in the anion sheet and four water molecules. Corner-sharing sodium octahedra form an infinite sheet similar in structure to anionic sheets formed by ZnO<sub>4</sub> and AsO<sub>4</sub> (Fig. 2). These cationic sheets are formed from sodium and water molecules and are connected to the anionic sheets through Na–O bondings. Note that the anionic sheet is far from planar. A side view of alternating anionic and cationic sheets is shown in Fig. 3.

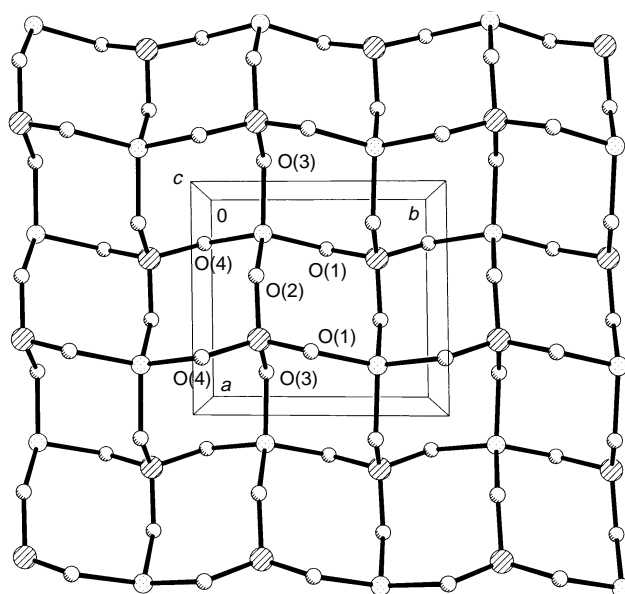
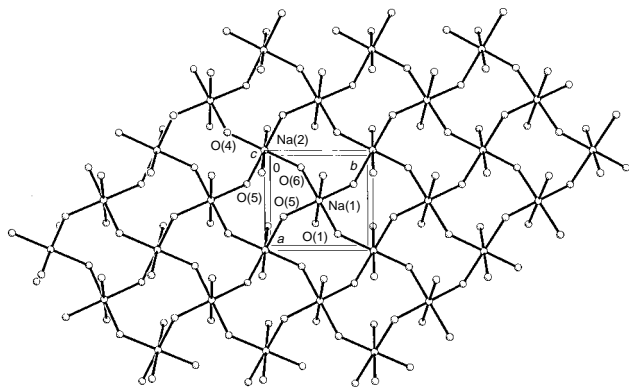
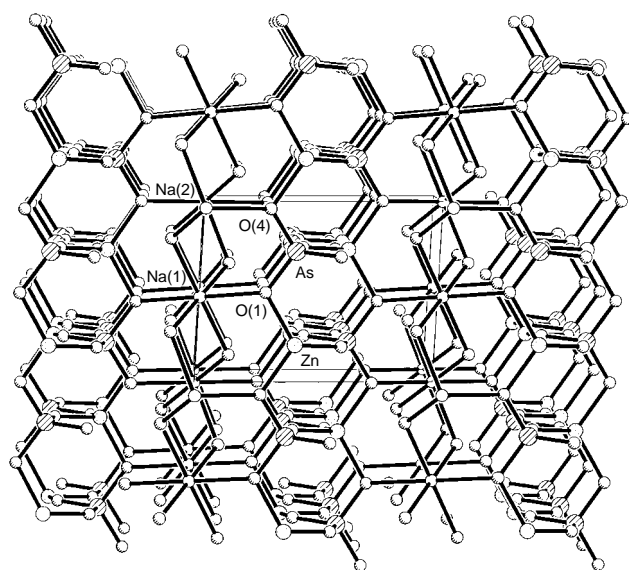


Fig. 1 Projection down the *c*-axis showing the anionic sheet built from ZnO<sub>4</sub> and AsO<sub>4</sub> tetrahedra. There are four different 4-rings, all of which have a center of inversion.



**Fig. 2** Projection down the *c*-axis showing the cationic sheet built from sodium octahedra. Two crystallographically unique sodium atoms are located at the unit cell origin and the face center which have inversion symmetry. Each ring contains four sodium cations and the center of each ring has inversion symmetry.



**Fig. 3** Side view (down the *a*-axis) of alternating anionic and cationic sheets

The circuit symbol, which enumerates the six distinct, smallest T-atom loop pathways<sup>10</sup> (including the central atom itself), can be written as (4<sup>4</sup>.6<sup>2</sup>) for all tetrahedral atoms. This type of tetrahedral atom configuration has never been previously known in either aluminosilicates or aluminophosphates. However, one chiral sodium zinc phosphate, NaZnPO<sub>4</sub>·H<sub>2</sub>O, which has similar formula to the title compound, but monohydrated, has half of the zinc cations (a quarter of tetrahedral atom positions) in such a configuration.<sup>11</sup> Our arsenate represents an extreme case in which all tetrahedral atoms exist in the (4<sup>4</sup>.6<sup>2</sup>) configuration. The synthesis of the title compound suggests that there could be novel phases with framework topology intermediate between NaZnPO<sub>4</sub>·H<sub>2</sub>O and the title compound. This is an interesting possibility considering that

NaZnPO<sub>4</sub>·H<sub>2</sub>O has a chiral symmetry and that chiral zeolites are very rare.<sup>12</sup>

Two other hydrated sodium zinc arsenates are known, both of which are tetrahedral framework structures. In Na<sub>6</sub>Zn<sub>3</sub>(AsO<sub>4</sub>)<sub>4</sub>·3H<sub>2</sub>O which is a relatively dense phase, one corner of AsO<sub>4</sub> is terminated with a pendant As=O bond.<sup>13</sup> Na<sub>6</sub>(ZnAsO<sub>4</sub>)<sub>6</sub>·8(H<sub>2</sub>O) is a sodalite analog with a cage structure.<sup>14</sup> Compared to this sodalite structure, it is observed that the increased hydration transforms the structure from the 3D framework sodalite structure into a lamellar phase. We have synthesized and characterized phosphate analogs of these two hydrated sodium zinc arsenates,<sup>4,15</sup> but so far, the phosphate analog of the title compound has not been prepared.

It's of interest that both anionic and cationic sheets have the same grid pattern and that the two types of sheets strictly alternate. The interlayer interaction between two sheets is through Na–O bondings. It is clear that the translational periodicity in one type of sheet and the geometrical feature of the sheet structure can be imprinted onto the other type of sheet, which can in turn replicate the original sheet. The good match between the sodium sheet and the zinc arsenate sheet implies that it may be difficult for other tetrahedral atoms such as P, or other alkali metal cations to replace Zn, As or Na while maintaining the same type of structure. This may explain why the phosphate analog of the title compound has not been synthesized so far.

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#### Footnotes and References

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† Crystal data for NaZnAsO<sub>4</sub>·2H<sub>2</sub>O, *M* = 263.31, space group *P* $\bar{1}$ , *a* = 5.6228(2), *b* = 6.1039(3), *c* = 7.9731 Å,  $\alpha$  = 86.655(1),  $\beta$  = 88.742(1),  $\gamma$  = 89.174(1)°, *V* = 273.09(2) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 3.202 g cm<sup>-3</sup>, clear thin plate, crystal size 0.25 × 0.10 × 0.017 mm, Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å,  $\mu$  = 10.541 mm<sup>-1</sup>,  $\theta_{\max}$  = 56°, *R*(*F*) = 0.0513, *wR*(*F*<sup>2</sup>) = 0.1210, GOF = 1.05 for 86 parameters and 1275 unique reflections with *I* > 2.0 $\sigma$ (*I*). CCDC 182/623.

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