

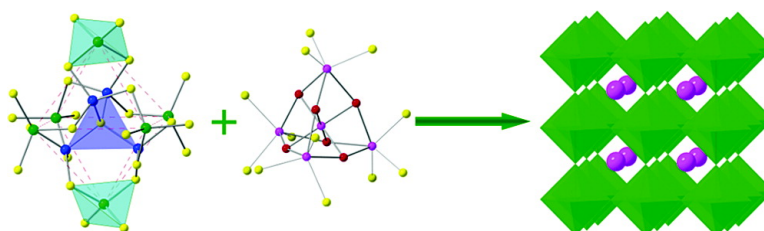
Communication

**Na(InS)(InS)·6H<sub>2</sub>O, a Zeolite-like Structure with Unusual Sn Tetrahedra**

Nanfeng Zheng, Xianhui Bu, and Pingyun Feng

*J. Am. Chem. Soc.*, **2005**, 127 (15), 5286-5287 • DOI: 10.1021/ja050281g • Publication Date (Web): 25 March 2005

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## Na<sub>5</sub>(In<sub>4</sub>S)(InS<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O, a Zeolite-like Structure with Unusual SIn<sub>4</sub> Tetrahedra

Nanfeng Zheng,<sup>†</sup> Xianhui Bu,<sup>‡</sup> and Pingyun Feng<sup>\*†</sup>

Department of Chemistry, University of California, Riverside, California, 92521, and Department of Chemistry and Biochemistry, California State University, 1250 Bellflower Boulevard, Long Beach, California, 90840

Received January 15, 2005; E-mail: pingyun.feng@ucr.edu

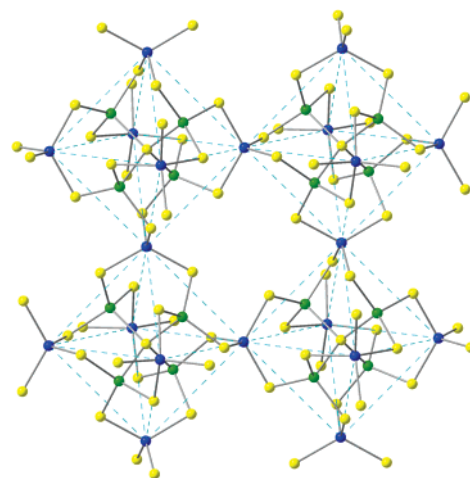
Open framework materials have been widely studied for applications in a variety of technological areas such as gas storage and separation, catalysis, sorption, and ion exchange.<sup>1–3</sup> Since 1989, open framework chalcogenides have attracted increasing attention because they are capable of integrating uniform porosity with semiconductivity and are promising candidates for applications ranging from shape-selective sensors to efficient visible-light photocatalysts.<sup>4–11</sup>

One of the guiding principles in the synthesis of chalcogenide clusters and their covalent lattices is Pauling's electrostatic valence rule that states the valence of an anion is exactly or nearly equal to the sum of electrostatic bond strengths to it from adjacent cations. The bond strength is defined as the ratio of the charge on a cation to its coordination number. In accordance with this rule, the tetrahedral S<sup>2-</sup> site is generally bonded to four divalent tetrahedral cations (e.g., Cd<sup>2+</sup>) so that the total valence from cations to the S<sup>2-</sup> site is 2.<sup>5–8</sup> Prior to this work, no open framework chalcogenide was known to contain S<sup>2-</sup> sites tetrahedrally bonded to four trivalent cations such as In<sup>3+</sup>.

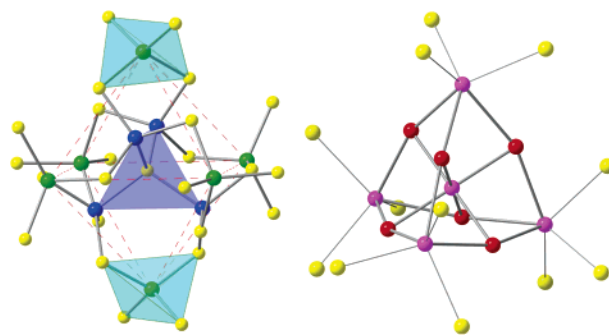
In our continual efforts to explore the rich synthetic and structural chemistry of metal chalcogenides, we are increasingly interested in developing materials with new bonding patterns and from building blocks other than commonly observed supertetrahedra (Figure S1). In addition to seeking novel properties associated with new structural features, this approach provides opportunities to prevent the interpenetration of lattices commonly observed in open framework chalcogenides with supertetrahedral clusters.<sup>5–8</sup>

Here we report the synthesis and structure of a new sodium indium sulfide hydrate, Na<sub>5</sub>(In<sub>4</sub>S)(InS<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O (denoted ICF-29). Despite its apparent compositional complexity, ICF-29 has a simple and elegant structural pattern, both for the host framework and extraframework clusters. This material also contains an unusual (SIn<sub>4</sub>)<sup>10+</sup> unit, an unprecedented feature among open framework solids. ICF-29 can be derived from the perovskite (CaTiO<sub>3</sub>) type structure with simultaneous substitutions of all atomic sites with larger building units (i.e., Ti<sup>4+</sup> by In<sub>4</sub><sup>10+</sup>, O<sup>2-</sup> by InS<sub>4</sub><sup>5-</sup>, and Ca<sup>2+</sup> by [Na<sub>5</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>5+</sup>) (Figure 1). Investigations into various properties of this material show that it is a wide band-gap semiconductor with photocatalytic activity for hydrogen production from aqueous solution.

To prepare ICF-29, In(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O (335 mg, 1.1 mmol), Na<sub>2</sub>S (252 mg, 3.2 mmol), TiS<sub>2</sub> (123 mg, 1.1 mmol), and distilled H<sub>2</sub>O (2.043 g) were placed into a 23-mL Teflon-lined stainless steel vessel. The resulting mixture was stirred for 10 min. The vessel was then sealed and heated at 150 °C for 4 days. After the autoclave was cooled to room temperature, light yellow rhombic dodecahedron-shaped crystals (60 mg, 27% yield based on indium) were recovered. The presence of TiS<sub>2</sub> is essential for the synthesis of ICF-29 since under hydrothermal condition it would hydrolyze and



**Figure 1.** Three-dimensional structure of ICF-29. Blue: In<sup>3+</sup>; yellow: S<sup>2-</sup>; green: In<sup>3+</sup> around tetrahedral S<sup>2-</sup>.



**Figure 2.** Two structural units in ICF-29. (Left) The six-connected [SIn<sub>4</sub>(InS<sub>4</sub>)<sub>6/2</sub>]<sup>5-</sup> cluster. The SIn<sub>4</sub> tetrahedron (blue) is at the center of the cluster with six InS<sub>4</sub> units surrounding it. Two InS<sub>4</sub> tetrahedra (cyan) are highlighted for clarity. Two different indium sites are colored in blue and green, respectively. (Right) The tetrahedral cluster [Na<sub>5</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>5+</sup>: purple, sodium; red, water; yellow, sulfur.

function as additional sodium-free sulfide source. Elemental analyses using the EDAX attachment on a scanning electron microscope showed no detectable Ti in crystals. The crystal structure of ICF-29 was solved from single-crystal data collected at 25 °C on a SMART CCD diffractometer.<sup>12</sup>

One unprecedented feature of ICF-29 is the presence of sulfur tetrahedrally bonded to four indium ions (Figure 2). To the best of our knowledge, such a bonding situation has not previously been observed in open framework chalcogenides. Other sulfur sites are bicoordinated. The tricoordinated sulfur site frequently observed in open framework chalcogenides does not occur in ICF-29. As discussed below, the absence of tricoordinated S<sup>2-</sup> sites is related to the occurrence of the unusual SIn<sub>4</sub> unit.

To satisfy Pauling's electrostatic valence rule, metal sites surrounding the tetrahedral sulfur are generally divalent (e.g., Cd<sup>2+</sup>,

<sup>†</sup> University of California.

<sup>‡</sup> California State University.

$\text{Zn}^{2+}$ ). The valence of the tetrahedral sulfur can also be balanced with two trivalent ions ( $\text{In}^{3+}$ ) and two monovalent ions ( $\text{Cu}^+$ ).<sup>7</sup> This helps to explain that known supertetrahedral sulfide clusters containing tetrahedral sulfur sites are actually in the ternary composition of  $\text{In-M-S}$  in which the tetrahedral sulfur atoms are coordinated to di- or mixed mono-/trivalent metal ions.<sup>8</sup> In contrast, the tetrahedral sulfur in ICF-29 is coordinated to four trivalent indium ions, in apparent violation of Pauling's rule. This bonding situation is very unusual in open framework chalcogenides; however, it can be rationalized with Brown's bond valence model and the overall  $\text{In}^{3+}$  coordination environment.<sup>13</sup> In ICF-29, the bond length from In to tetrahedral S is 2.55 Å, significantly longer than the typical In-S bond distance (2.44 Å). As a result, the valence sum for the tetrahedral S is 2.24 (instead of 3 according to Pauling's rule), close to the expected value of 2.<sup>13</sup> The lengthening of the bond (or decreased bond valence) from In to tetrahedral S is because the other three In-S bonds all involve underbonded bicoordinated  $\text{S}^{2-}$  sites and therefore have higher-than-usual bond valences. In comparison, in regular sulfide open frameworks (e.g., supertetrahedra-based structures), metal sites bonded to tetrahedral S sites are also bonded to tricoordinated  $\text{S}^{2-}$  sites, and as a result, the bond valence is more evenly distributed among four metal-S bonds.<sup>8</sup> Under this situation, the unusual tetrahedral unit such as  $\text{SIn}_4$  is unlikely to occur.

One known sodium indium sulfide phase is  $\text{NaInS}_2$ , a layered structure with anionic layers built from edge-sharing  $\text{InS}_6$  octahedra and  $\text{Na}^+$  cations sandwiched between the layers.<sup>14</sup> In contrast, all  $\text{In}^{3+}$  sites in ICF-29 are tetrahedrally coordinated to four sulfurs. Through corner-sharing sulfurs,  $\text{InS}_4$  tetrahedra are connected into an extended framework. ICF-29 can be regarded as a structure based on the perovskite ( $\text{CaTiO}_3$ ) type in which  $\text{TiO}_6$  octahedra are interconnected into a three-dimensional framework with  $\text{Ca}^{2+}$  sitting within cavities.<sup>15</sup> In ICF-29, the corresponding six-connected units are large  $[\text{SIn}_4(\text{InS}_4)_{6/2}]^{5-}$  clusters, while the cavities are occupied by tetrahedral  $[\text{Na}_5(\text{H}_2\text{O})_6]^{5+}$  clusters.

As illustrated in Figure 2,  $\text{SIn}_4$  tetrahedron is located at the center of each six-connected  $[\text{SIn}_4(\text{InS}_4)_{6/2}]^{5-}$  cluster. Every pair of indium atoms from this tetrahedron is shared with one  $\text{InS}_4$  tetrahedron. There are a total of six  $\text{InS}_4$  tetrahedra surrounding the core  $\text{SIn}_4$  tetrahedron, forming a large  $[\text{SIn}_4(\text{InS}_4)_{6/2}]^{5-}$  cluster. These  $[\text{SIn}_4(\text{InS}_4)_{6/2}]^{5-}$  clusters function as building blocks and are connected through six peripheral  $\text{InS}_4$  tetrahedra into an extended framework.<sup>16</sup> Because the corner  $\text{InS}_4$  tetrahedron is shared between two adjacent clusters, the overall formula for the framework becomes  $[\text{SIn}_4(\text{InS}_4)_{6/2}]^{5-}$ . No centrosymmetry is associated with each cluster in ICF-29 due to the existence of  $\text{SIn}_4$  tetrahedron at its core. As a result, ICF-29 possesses a noncentrosymmetric cubic unit cell with the axial length of 18.21 Å.

The extraframework space is occupied by  $[\text{Na}_5(\text{H}_2\text{O})_6]^{5+}$  clusters. Each  $[\text{Na}_5(\text{H}_2\text{O})_6]^{5+}$  cluster is trapped within the cavities formed by eight  $[\text{SIn}_4(\text{InS}_4)_{6/2}]^{5-}$  clusters. As illustrated in Figure 2, the  $[\text{Na}_5(\text{H}_2\text{O})_6]^{5+}$  cluster is tetrahedron-shaped with four  $\text{Na}^+$  at the corners and the fifth  $\text{Na}^+$  at the center of the tetrahedron. Six water molecules are located about halfway on each edge of the tetrahedron. The central  $\text{Na}^+$  is bonded to these six  $\text{H}_2\text{O}$  molecules with an ideal octahedral geometry. Each  $\text{Na}^+$  ion sitting at the corner of the tetrahedron is bonded to three  $\text{H}_2\text{O}$  molecules and three S atoms from the In-S framework.

Extraframework  $\text{Na}^+$  cations are highly ordered in contrast with the disorder in other ICF-*n* compounds.<sup>11</sup> Therefore, ICF-29 has a

low ionic conductivity. At room temperature and under relative humidity less than 50%, its conductivity is smaller than  $10^{-8}$   $\text{ohm}^{-1}\cdot\text{cm}^{-1}$ . When excited at 360 nm at room temperature, ICF-29 exhibits emission with a strong peak at 434 nm and a shoulder peak at 585 nm. Upon being heated under vacuum, ICF-29 is stable up to 270 °C. Variable temperature powder diffraction showed that there is phase transition from ICF-29 to  $\text{NaInS}_2$  starting from 270 °C and completed at 380 °C. It is particularly interesting that ICF-29 has a band gap of 3.2 eV and shows photocatalytic activity under UV light for hydrogen generation from an aqueous solution containing  $\text{Na}_2\text{SO}_3$  as sacrificial agent even in the absence of any cocatalyst such as Pt.<sup>17</sup> Given that no such activity can be detected with the dense  $\text{In}_2\text{S}_3$  phase, the framework structure of ICF-29 may be related to the creation of photocatalytic activity.

**Acknowledgment.** We thank for the support of this work CSULB (X.B.), the NSF (P.F.), Beckman Foundation (P.F.), and the donors of the Petroleum Research Fund (administered by the American Chemical Society) (X.B. and P.F.). P.Y. is an Alfred P. Sloan research fellow and Camille Dreyfus Teacher-Scholar.

**Supporting Information Available:** An illustration of supertetrahedral clusters (Figure S1, PDF) and 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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JA050281G