

# Hsichengia: A 4,6-Connected Trigonal Structural Pattern in Space Group $P3m1$ <sup>1</sup>

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**Abstract**—A novel 4,6-connected network, called Hsichengia, is described. The novel network lies in the trigonal space group  $P3m1$  (no. 156), with  $a = b = 3.447$  Å and  $c = 12.948$  Å; these lattice parameters were derived assuming Fe–S composition. It implies a binary  $AB_2$  stoichiometry in which the 6-connected A (Fe) atoms have octahedral configuration, and the 4-connected B (S) atoms have tetrahedral configuration. The Hsichengia network seems to be very closely related to the layered  $MoS_2$  structure-type, in which puckered  $MoS_2$  layers composed of octahedral Mo centers and trigonal–pyramidal S centers are held together by weak van der Waals forces normal to the  $a$  and  $b$  directions where the  $MoS_2$  layers extend. Thus the Hsichengia network can be generated from the  $MoS_2$  lattice by the formation of disulfide (S–S) bridges between particular layers, thereby creating a 3-dimensional network from a 2-dimensional layered structure, so that the S atoms are transformed from 3-connected trigonal–pyramidal coordination into fully 4-connected tetrahedral coordination. The Wells point symbol for the Hsichengia network is given by  $(4^6 6^6)(4^3 6^3)_2$ , and it is thus seen to have the translated Schläfli symbol given as  $(5, 4^{2/3})$ . The latter is identical to that intrinsic to the well-known mineral structure of the pyrite network,  $FeS_2$ , with the corresponding Wells point symbol  $(5^{12})(5^6)_2$ . Therefore, the Hsichengia network may be regarded as a topological isomer of the pyrite network, where topological isomerism is defined as occurring between unique networks possessing the same Schläfli symbol. Phase transformation between the two topological isomers is possible.

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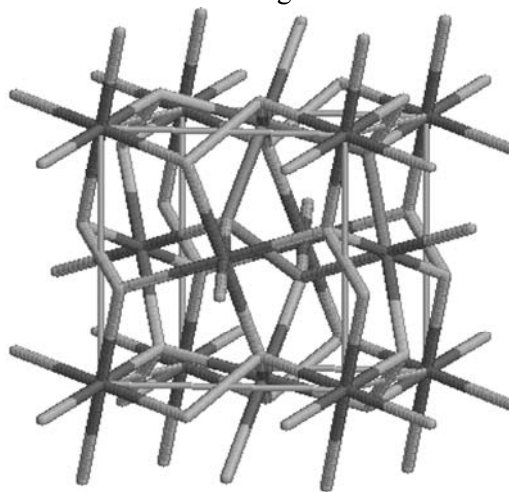
In this communication we describe a novel 4,6-connected inorganic crystal structure with the stoichiometry  $AB_2$  which is derived from the known layered  $MoS_2$  crystal structure (shown in Fig. 1 as slightly tilted at an angle of  $45^\circ$  from the  $ab$  plane) by joining adjacent trigonal pyramidal S atoms in adjoining puckered  $MoS_2$  layers via simple disulfide (–S–S–) bridges. It is known that disulfide bridges underlie a structural motif of proteins which constitute a biologically important class of molecules. We have found no published data on disulfide bridges in inorganic structures.

The novel inorganic structure was called Hsichengia.<sup>2</sup> It belongs to the trigonal space group  $P3m1$  (no. 156) and may be regarded as a topological isomer of the pyrite structure type with the following

<sup>1</sup> The text was submitted by the author in English.

<sup>2</sup> The name Hsichengia was given in honor of the designer Hsi-cheng Shen who is the wife of M.J. Bucknum and who designed this network in an artistic frenzy in 2002 in Milledgeville, Georgia, USA.

unit cell parameters:  $a = b = 3.447$  Å,  $c = 12.948$  Å. Table contains the coordinates of 9 atoms defining a unit cell of Hsichengia, three of which are octahedral iron atoms, and the remaining six atoms are tetrahedral sulfur atoms. The bond angles between octahedral



**Fig. 1.** A view of the  $MoS_2$  structure-type tilted by  $\sim 45^\circ$  from the crystallographic  $ab$  plane.

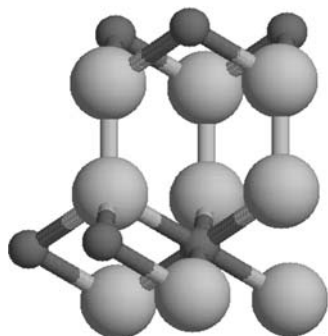


Fig. 2. A view of the trigonal Hsichengia network approximately tilted by  $45^\circ$  from the crystallographic  $ab$  plane.

|     | $p$   |       |       |       |       |       |     |
|-----|-------|-------|-------|-------|-------|-------|-----|
| $n$ | 3     | 4     | 5     | 6     | 7     | 8     | ... |
| 3   | $t$   | $o$   | $i$   | (3.6) | (3.7) | (3.8) |     |
| 4   | $c$   | (4.4) | (4.5) | (4.6) | (4.7) | (4.8) |     |
| 5   | $d$   | (5.4) | (5.5) | (5.6) | (5.7) | (5.8) |     |
| 6   | (6.3) | (6.4) | (6.5) | (6.6) | (6.7) | (6.8) |     |
| 7   | (7.3) | (7.4) | (7.5) | (7.6) | (7.7) | (7.8) |     |
| 8   | (8.3) | (8.4) | (8.5) | (8.6) | (8.7) | (8.8) |     |
| ... |       |       |       |       |       |       |     |

Fig. 3. Wells topology map of regular structures.

vertices (ideal angle  $90^\circ$ ) bonded to those having tetrahedral configuration (ideal angle  $109.47^\circ$ ), will be a compromise between these ideal values. Assuming the  $\text{FeS}_2$  composition of the Hsichengia network, we selected  $\text{SFeS}$  bond angles of either  $81^\circ$  or  $99^\circ$ ,  $\text{SSFe}$  bond angles of  $119^\circ$ , and  $\text{FeSFe}$  bond angles of  $99^\circ$ . The bond angles in the topologically isomeric pyrite structure type are closer to ideal values than those in the Hsichengia network, and the angular strain in the latter may be responsible for the existence of one isomer (pyrite) rather than other (Hsichengia) despite topological, bonding, and compositional similarities between these structures.

Figure 2 shows a view of the Hsichengia lattice, in which the iron atoms are shown as dark balls and sulfur atoms are shown as light balls; the structure is tilted by approximately  $45^\circ$  from being parallel to the  $ab$  plane of the trigonal structure. Note the presence of tetragons and hexagons in the structure, which can be traced from the 6-connected octahedral Fe vertices (dark) and 4-connected tetrahedral S vertices (light) in

the net. It is seen that there are bonds between 4-connected vertices (so-called 4–4 bonds or disulfide  $-\text{S}-\text{S}-$  bridges) and between 4-connected and 6-connected vertices (so-called 4–6 bonds). However, there are no any 6–6 linkages in the network. The 4–4 linkages belong to the hexagons in the structure (4–4–6–4–4–6), and the 4–6 bonds belong to both tetragons (4–6–4–6) and hexagons (4–6–4–4–6–4). It would be possible to introduce 6–6 linkages into the Hsichengia net by forming 6-connected metal–metal bonded layers of arbitrary thickness that are terminated by ordinary 4–6 bonding already present in Hsichengia. Thus 6–6-bonded metal layers of arbitrary thickness [constituting a primitive cubic sublattice of the (4, 6) topology] could be held to each other by  $-\text{S}-\text{S}-$  disulfide linkages between the metal layers, where S atoms are alternately joined to metal atoms in the adjacent layers via 6–4–4–6 bonds.

By tracing the polygonal circuits over the Hsichengia network, we can formulate Wells point symbol for it. Assuming an  $\text{AB}_2$  stoichiometry, we assigned the Wells point symbol  $(4^6 6^6)(4^3 6^3)_2$  for Hsichengia. As described previously in some detail [1], this Wells point symbol can be translated into a weight-average polygonality  $n$  and a weight-average connectivity  $p$  to yield the corresponding Schläfli symbol for the network  $(n, p)$ . The Schläfli symbol for Hsichengia is therefore  $(5, 4^{2/3})$ . A topology map of all structures, already described in some detail previously [1], is shown in Figure 3. The network therefore can be mapped into this Schläfli space and falls into the vicinity of the (5,4) and (5,5) entries. The latter corresponds to a three-dimensional polyhedron that Wells enumerated years ago in his revolutionary monograph on three-dimensional nets and polyhedra, and represents a continuation of the sequence (3,3), given as the Platonic solid known as the tetrahedron, and the two-dimensional tessellation known as the square network (4,4), into fully three-dimensional space [2].

Wells has already pointed out the Wells point symbol for the compositionally and stoichiometrically related  $\text{Fe}-\text{S}$  structure known as pyrite ( $\text{FeS}_2$ ), as given by  $(5^{12})(5^6)_2$  [2]. The pyrite structure type is an elegant Catalan inorganic structure-type, in which all smallest circuits about the 4-connected tetrahedral vertices (S atoms), and 6-connected octahedral vertices (Fe atoms), are pentagons. The pyrite network is shown in Fig. 4.

The Schläfli symbol that can be translated from  $(5^{12})(5^6)_2$  is therefore given as  $(5, 4^{2/3})$  [1]. Quite in contrast, the Hsichengia network, which consists of 4-connected (tetrahedral) and 6-connected (octahedral) vertices forming both tetra- and hexagonal circuits, is topologically a Wellsean [1] network with the Wells point symbol  $(4^6 6^6)(4^3 6^3)_2$ . Yet, despite the fact that pyrite is a Catalan network and the Hsichengia network is Wellsean [1], their translation into the corresponding Schläfli symbol yields the same polygonality and connectivity values,  $(n, p) = (5, 4^{2/3})$ . Therefore, the pyrite structure and Hsichengia are topologically isomeric networks with the same Schläfli symbol.

Wells has enumerated many topologically isomeric networks, including those in the series of structures given by the Schläfli symbols  $(7, 3)$ ,  $(8, 3)$ ,  $(9, 3)$ , and  $(10, 3)$  [2]. In separate work on organic networks [3] it was pointed out that there is a possibility of myriad examples of topological isomerism between infinite families of Catalan graphite–diamond hybrids [4] and various hexagonites described by Karfunkel and Dressler [5] and Bucknum [3].

It is not clear why Nature prefers to adopt the Catalan pyrite structure for  $\text{FeS}_2$ , though an alternative structure of Hsichengia in the same  $\text{AB}_2$  stoichiometry and with the same 4- and 6-connected coordination environments is evidently accessible. One reason for the preference of pyrite structure for  $\text{FeS}_2$  may be that Nature prefers regularity in topological characteristics of its structures whenever possible. This might explain why graphite  $(6, 3)$  and diamond  $(6, 4)$  have been known structures of carbon for millennia, while only very recently (in 1985) topologically Archimedean fullerene structures of carbon allotropy were discovered [6]. There are still examples of natural Wellsean networks such as phenacite ( $\text{Be}_2\text{SiO}_4$ ) [2, 7] and its isostructural relatives including  $\text{Ge}_3\text{N}_4$  and  $\text{Si}_3\text{N}_4$  [8–11].

Another contributing reason for preference of the pyrite structure over that of Hsichengia, may be relative angular strain in the lattices (see above). From the proposed  $\text{FeS}_2$  composition of Hsichengia it is quite clear that the bond angles in pyrite for identical tetrahedral and octahedral coordination entities are closer to ideality than those in Hsichengia (see table).

Of course, the existence of topological isomerism suggests that phase transition of pyrite to the Hsichengia structure type may be possible under some

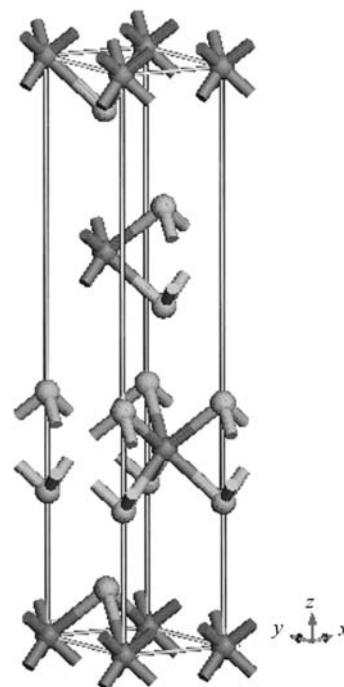


Fig. 4. A view of the pyrite network  $\text{FeS}_2$ .

pressure and temperature conditions. Probably, *ab initio* energy optimization of the structures is necessary to clarify the nature of such phase transition and understand why one structure is preferred over the other on a quantitative level.

Thus a novel hypothetical network has been proposed with the  $\text{AB}_2$  stoichiometry, which belongs to the trigonal space group  $P3m1$  (no. 156) and has 9 atoms in a unit cell ( $3A + 6B$ ). The hypothetical network can be constructed from the layered mineral

Trigonal fractional crystallographic coordinates of Hsichengia ( $P3m1$ ); lattice parameters:  $a = b = 3.447 \text{ \AA}$ ,  $c = 12.948 \text{ \AA}$

| Atom          | $x/a$ | $y/b$ | $z/c$  |
|---------------|-------|-------|--------|
| $\text{Fe}^1$ | 2/3   | 1/3   | 0.167  |
| $\text{Fe}^2$ | 1/3   | 2/3   | 0.833  |
| $\text{S}^3$  | 0     | 0     | -0.082 |
| $\text{S}^4$  | 0     | 0     | 0.082  |
| $\text{S}^5$  | 1/3   | 2/3   | 0.251  |
| $\text{S}^6$  | 2/3   | 1/3   | 0.584  |
| $\text{S}^7$  | 1/3   | 2/3   | 0.416  |
| $\text{S}^8$  | 2/3   | 1/3   | 0.749  |
| $\text{Fe}^9$ | 0     | 0     | 1/2    |

structure of MoS<sub>2</sub> by bonding trigonal pyramidal S atoms in the adjacent MoS<sub>2</sub> layers to each other through disulfide bridges.

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