

Supertetrahedra in Sulfides: Matter against Mathematical Series?

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In the Beginning was the Game! To Perforate Dense Matter

Even now, Cronstedt^[1] could not imagine the consequences of his discovery of the natural zeolite stilbite, the first porous solid to have been found by a chemist. At least as a first step, most of the consequences relate to the curiosity of chemists and their need to do better and better, just for the challenge. But how many surprises would the players uncover?

The mimicking of nature began in the middle of the 19th Century with the first synthetic homologue of natural zeolite^[2] (levynite), formed from a mixture of dense phases (Al₂O₃ and SiO₂) in an alkaline medium. In the resulting phase, alkaline ions and water played the role of a cutter (template) for the original dense structures, and the elimination of water (through heating) gave rise to the porosity of the structure. This concept was further developed^[3] when organic molecules (mainly quaternary ammonium ions and amine groups) replaced the alkaline ions. The modular character of the length of the carbon chain led to an explosion of new porous solids with increasing pore dimensions, the inorganic skeleton remaining mainly composed of AlO₄, SiO₄ and, additionally, PO₄ tetrahedra when the porous aluminophosphates were discovered.^[4]

Along with many variations developed around that theme, some other breakthroughs occurred later, which mainly concerned oxides^[5] and, to a lesser extent, oxyfluorides.^[6] The introduction of six-coordinate cations into the frameworks (rather than four),^[7] the discovery of magnetic porous solids^[8] where transition-metal atoms fully replaced aluminum in the skeleton, the first studies on the mechanisms of the formation of these solids,^[6c,9] and so on. The aim of such developments was to increase the size of the pores,^[10] mainly by adjusting the characteristics of the template, for improved applications of this family of solids (such as, catalysis, gas separation, nanoreactors). One of the last breakthroughs concerned the discovery of porous sulfides, which possess supertetrahedral frameworks, and about which this highlight is dedicated.

The Porous Sulfides and Mathematical Extrapolation

The known classes of open-framework materials are overwhelmingly dominated by oxide or mixed oxide/fluoride matrices. In 1989, however, Bedard et al.^[11] proposed to extend this class of materials to metal sulfide compounds by using the same principle of perforating dense matter with the use of organic templates. Two recent reviews^[5,12] report the progress with these topics up to 1999.

From the point of view of crystal chemistry, the choice of sulfides presents many advantages: a) The larger ionic radius of the S²⁻ ion, compared to those of oxide and fluoride ions, favors tetrahedral coordination for the cations and

therefore allows the discovery of sulfide homologues of zeolites, b) in the eventuality of such structures, the higher polarisability of the S²⁻ ion implies more flexibility for the T-S-T angles that exist between tetrahedra (109–161°), when compared to those with oxides (140–145°) and, consequently, more flexible frameworks that better accommodate the shape of the template and, more surprisingly, c) the arrangement of the tetrahedra in the starting dense matter remains unchanged.

In principle (Figure 1 a–d), the perforation of a dense phase (here ZnS or sphalerite) by templates can create holes that are surrounded by groups of, for example, four- (T2), ten- (T3), or twenty- (T4) corner-sharing tetrahedra, according to the size and the charge of the template. Whatever the arrangement of these superclusters, the supertetrahedra obey some mathematical rules. According to O'Keeffe et al.,^[13] the number of tetrahedra (T atoms) in a T_p supertetrahedron is the pth tetrahedral number $t_p = p(p+1)(p+2)/6$. The number of distinct vertexes (S atoms) in one supertetrahedron is t_{p+1} . In a continuous framework, each of the four outmost vertexes of a supertetrahedron is shared with another supertetrahedron, so that the overall composition is T_xS_y with $x = t_p$ and $y = t_{p+1} - 2$. Therefore, the compositions of T2, T3, and T4 supertetrahedra are T₄S₈, T₁₀S₁₈, and T₂₀S₃₃, respectively.

The first T2 structure appeared in 1987,^[14a] but the interest in supertetrahedra began after the work of Yaghi et al.^[14b] who showed that the adamantanoid cluster (NMe₄)₄Ge₄S₁₀ reacts with manganese acetate in water at room temperature to give a three-dimensional

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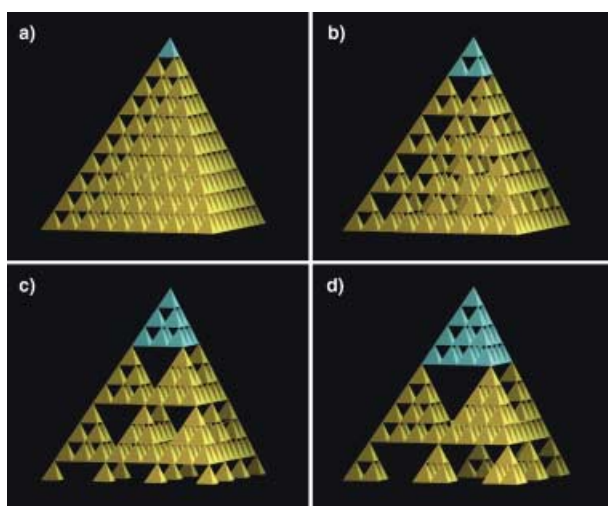


Figure 1. The principle of building supertetrahedra from the dense sphalerite structure: a) A part of the sphalerite structure limited to a large tetrahedron corresponding to an edge of ten primitive tetrahedra (in blue); b) assembly of T2 supertetrahedra with the same sphalerite topology (the supertetrahedron, in blue, contains four metal centers); c) assembly of T3 supertetrahedra built on the same principle; d) assembly of T4.

(3D) network $((\text{NMe}_4)_2\text{MnGe}_4\text{S}_{10})$; several similar compounds appeared later.^[14c-e] The game was then to increase the size of the supertetrahedra, with the risk that enlarging the size of the hole was advantageous for the undesired interpenetration of two identical subnetworks, which was indeed frequently observed. However, using an incrementation strategy, the Yaghi and O’Keeffe research group isolated^[15a,b] three non-interpenetrating indium sulfides, ASU-31, 32, and 34, with T3 supertetrahedra (ASU = Arizona State University), while interpenetrating examples were also discovered.^[15c] The same group^[13] and another^[16] recently succeeded in the third incremental step (T4); the T4 cluster $[\text{M}_4\text{In}_{16}\text{S}_{33}]^{10-}$ containing in this case a divalent metal M (M = Mn, Co, Zn, Cd) as well as indium. With such discoveries, there was hope that this series might be continued, based on the same mathematical rules, for example, $\text{T}_{35}\text{S}_{54}$, $\text{T}_{56}\text{S}_{82}$, and so on. The edge of the supertetrahedra corresponds to n times the S–S distance in the primitive tetrahedron and the size of the cavity increasing accordingly.

Moreover, these extended frameworks, the series of which has been augmented recently with networks containing $\text{M}^{4+}/\text{M}^{3+}$ ions,^[17] can present new structure types (T4)^[16] but are very often the upper homologues of well-known basic topologies (aristotypes), such as

diamond (T3),^[15c] sodalite (T2, T3),^[15a] cristobalite (T2, T3, T4),^[13,14a,15b] or CrB_4 (T2, T3),^[15a] and provide nice examples of the concept of scale chemistry^[18] (“the larger the bricks, the larger the pores”). It is worth noting that the

flexibility of the T-S-T angles compared to the rigidity of the corresponding T-O-T angles leads, in these superframeworks, to contracted versions of the aristotypes.^[13,15a]

Breaking Off

T5, the next term in the series, was much sought after. Two recent papers^[19,20] described its nature, but the results mark a break from the previous evolution. The striking feature common to the two structures concerns the T5 cluster itself. Whereas the lower cluster homologues are complete, one core atom is missing in both T5 structures (Figure 2a), and the formula corresponds to $\square_1\text{T}_{34}\text{S}_{54}$ (\square = missing atom). Moreover, when T5 is the only type of cluster in the structure,^[20] the solid is two-dimensional (2D). Surprisingly, in the second solid,^[19] 3D character is preserved because of the presence, for the first time, of two types of superclusters, T3 and T5, linked at their corners (Figure 2b). This clearly indicates that T5 represents a limit for the

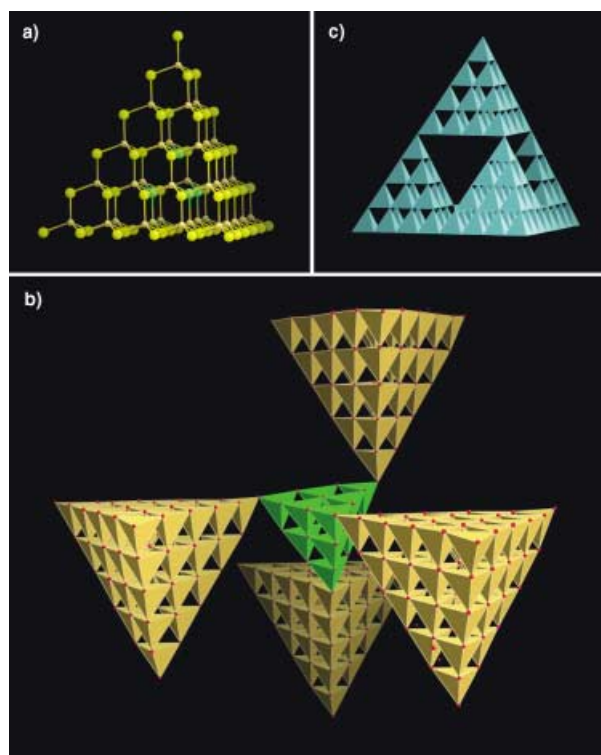


Figure 2. a) Ball-and-stick representation of the defect-containing T5 cluster; the four sulfur atoms surrounding the vacancy are indicated in green; b) ordered arrangement of T3 and T5 supertetrahedra in the structure of ref. [19]; c) the T4,2 cluster.

initial evolution, an interesting problem which needs to be addressed to answer the fundamental questions regarding the primitive evolution and the reasons for the break in the series.

And After the Game, Questions...

Of course, the first question concerns the defective nature of the T5 topology, since both examples given above have the same characteristics. It is evident that there is no obvious reason to explain the behavior, but some suggestions can be offered.

The first reflection takes into account some chemical observations. Looking at the evolution of the nature of the cations involved in the T_n series, T2 involved a mixture of tetra- and divalent ions (Ge^{4+} and Mn^{2+} , $(\text{NMe}_4)_2\text{MnGe}_4\text{S}_{10}$),^[14b] T3 contained exclusively trivalent metal ions (In^{3+} , ASU-32: $\text{In}_{10}\text{S}_{18}(\text{C}_{11}\text{H}_{24}\text{N}_2)_3(\text{H}_2\text{O})_7$),^[15] T4 introduced divalent metal ions (mainly Cd^{2+}) as well as In^{3+} (CdInS-44 : $\text{Cd}_4\text{In}_{16}\text{S}_{33}(\text{C}_{10}\text{H}_{28}\text{N}_4)_{2.5}(\text{H}_2\text{O})_{20}$),^[13] while the pure T5 structure [$\text{Cd}_6\text{In}_{28}\text{S}_{54}\text{-}\{(\text{CH}_3)_4\text{N}\}_{12}(\text{HSCH}_2\text{COOH})_{2.5}\}$]^[20] leads to a trend in the formal charges for the clusters, as follows: $[\text{T2}]^{2-}$, $[\text{T3}]^{6-}$, $[\text{T4}]^{10-}$, and $[\text{T5}]^{12-}$. The progressive introduction of lower valences, which limits the expansion of the negative charge of the cluster (a charge too negative would render the solid unstable), is in agreement with the upper infinite limit corresponding to the neutral solid CdS with the sphalerite structure. For T5, if a vacancy was not present, the negative charge would be too small ($[\text{T5}]^{10-}$ or $[\text{T5}]^{9-}$ if the vacancy is occupied by Cd or In, respectively). It seems that, once more, the building unit accommodates its condensation (here by the creation of a defect in the structural building unit) according to the charge density of the template, the precipitation being explained either by equalization of the electronegativities of the groups^[6c,d] or by the host-guest charge-density-matching principle.^[21] However, the latter does not help to explain (when assimilating the charge density to the C/N ratio of the template) the evolution in the whole series.

A more interesting evolution, already noted by Feng et al.,^[19] relates to

the negative charge per metal site within the overall framework of the cluster, which decreases in steps from T2 (−1) to T5 (−0.35) via T3 (−0.6) and T4 (−0.5). This could be an interesting indicator for further synthesis.

However, it is not only electronic reasons that explain the evolution and the breaking of the trend; the chemical conditions also play a major role. The novel material^[19] that contains both T3 and T5 morphologies (noting that $[(\text{NMe}_4)_2\text{MnGe}_4\text{S}_{10}]$ is a combination of T1 and T2) provides a good illustration of this point. Indeed, the comparison between the synthesis conditions of the latter and ASU-32, which only contains T3 clusters, are exactly the same (identical concentrations, ratios, and template). Only temperature and time differ (135 °C and 5 days for ASU-32; 190 °C and 16 days for $[(\text{NMe}_4)_2\text{MnGe}_4\text{S}_{10}]$) which seems to show that increasing time and temperature favor larger clusters. This interesting feature poses questions about the mechanism of formation of these supertetrahedra. Any tentative explanation of the formation requires a thorough in situ study of the succession of the appearance of these phases, as was carried out by Parise^[22] on Ge_4S_{10} -based solids.

The last question concerns templates and their exact role. If it is obvious that their shape, combined with the flexibility of the T-S-T angles, directly influences the shape and the dimensions of the cavities, the situation is more complicated than for aluminophosphates.^[6c,d] Is there a direct relation between their charge and the size of the cluster? Do they play the role of structure-directing or space-filling agents, or both? The fact that all the solids lose their templates proportionally with temperature, with no observed plateau corresponding to the empty solid, left the question open. It is noteworthy that, before the recent paper of Feng^[24] and the description of the porous solid UCR20, previous papers did not mention the porosity of these solids, despite the large dimensions of all the cages; the framework representing between 20 and 45% of the total space.

Open Windows

These concern both fundamental research and applications. Defective T5 clusters with one metal vacancy may tempt chemists to consider them as the first term in a new series, after the break, by increasing the number of vacancies with the number of metallic sites in the cluster. As noted by Feng et al.,^[19] one might have imagined until recently that the game may be continued by creating “a whole family of coreless nanoclusters with sizes larger than T5”. The series would be continued by a T6 cluster with a missing T2 core ($[\square_4\text{M}_{52}\text{X}_{84}]$), a T7 cluster with a missing T3 core ($[\square_{10}\text{M}_{74}\text{X}_{120}]$), a T8 cluster with a missing T4 core ($[\square_{20}\text{M}_{100}\square_1\text{X}_{164}]$), and so on, with the aim of creating clusters with inter- and intracuster pores. However, although the idea is brilliant, the intracuster concept is not so obvious since, even if there are 4, 10, and 20 metallic defects, they do not create real internal space (only the volume of a cation) and the series must reach T8 before an anionic vacancy with an internal pore the same diameter as a sulfur atom is achieved. But conceptually, the approach was very interesting, even if it will not reach the fascinating dimensions of the Mo oxide-based hollow spheres recently described by Müller et al.^[23]

This was true until very recently, but a discovery by Yaghi and O’Keeffe once more breaks the series.^[24] Very recently, they described a super-supertetrahedral cluster with 214 atoms and 80 tetrahedra. The topology is the same as a T2 cluster (which contains four single tetrahedra), but this time, each single tetrahedra is replaced by T4 supertetrahedra. The latter leave an octahedral vacancy at the center of the cluster with a volume of 1855 \AA^3 ! This striking feature requires a change in the notation of the supertetrahedra by using two numbers p and q . Specifically, $T_{p,q}$ will be used to describe a T_q supertetrahedron of T_p supertetrahedra. The first term of this new series (Figure 2c) is therefore T4,2.

In addition to the numerous ideas stated by Ozin^[12] for biological applications, the potential applications of these solids are also evident. First of all, they are ion exchangers (except for two examples^[13,24]) and can accept mono-

and divalent cations in good yield. This means that, even if no porosity measurements were performed, the cavities containing the templates are accessible. However, the most attractive application, which renders these solids close to nanomaterials, concerns their semiconducting character (a band gap of 3 eV) and it is meritorious of Li et al.^[20] to have discussed this point. Indeed, these materials are, in many ways, far superior to colloidal nanoparticles (classical quantum dots). The periodical arrangement of the clusters (dots) and cavities (antidots) in the crystal presents many advantages compared to the randomly distributed colloids, particularly in providing opportunities for studying the collective physical phenomena attributed to interactions between individual dots (energy transfer, excitonic splitting, etc.), the regular distance between the dots giving rise to strong interdot coupling. The first measurements by Li show that the density of states near the top of the valence band, larger than that of normal III–V semiconductors, is dominated by sulfur lone-pair orbitals. This situation gives rise, according to Li, to a small band dispersion, and the band-edge transitions are sharp, which will be useful for efficient laser and solar devices. This unusual family of solids is therefore promised a brilliant future, despite the unresolved questions concerning their formation.

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