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# The $CdSO_4$, rutile, cooperite and quartz dual nets: interpenetration and catenation

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Dedicated to Sten Andersson for his scientific contribution to Solid State and Structural Chemistry

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**Abstract**

The $CdSO_4$ and quartz nets are described as tilings of generalized tetrahedra $[6^2 \cdot 8^2]$. The $CdSO_4$ net shares with the diamond net the property of having the minimum number (2) of vertices in the topological repeat unit of a 4-coordinated net. It is self dual which explains its propensity to occur self-interpenetrating in crystalline frameworks. The rutile ($TiO_2$) and cooperite (PtS) nets are closely related to that of $CdSO_4$ which explains why they also often occur interpenetrating. The dual of the quartz net is a net formerly described as "dense net" and is carried by a tiling $[7^4]$. The quartz dual net cannot self-intergrow without degradation of symmetry. Two intergrown quartz nets have half their rings not catenated and the other half doubly catenated. Attention is called to some other simple nets that like that of cooperite have mixed tetrahedral and square coordination.

*Keywords:* Nets; Tilings; Duals; Intergrowth; Catenation; Quartz; Rutile; Cooperite

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## 1. Introduction

Some years ago one of us introduced [1] the 4-coordinated net named for $CdSO_4$ and a net simply called "dense net" which we now prefer to call the "quartz dual" net. Here we describe some newly discovered properties of these nets, and also describe a simple connection of the $CdSO_4$ net to those of the rutile ($TiO_2$) and cooperite (PtS) structures [2] that explains why these three often occur as pairs of intergrown nets.

We find it useful to discuss nets in terms of tilings of space by generalized polyhedra (*cages*) in which there may be vertices at which only two edges meet—the vertices and edges of the tilings correspond to those of the net [3,4].

We briefly define some essential terms: *Natural tilings* are tilings of maximum symmetry in which the faces of the tiles are what we call *essential rings* [5]. Essential rings have the property that they are not the sum of smaller rings; a *ring sum* of two or more rings being defined as usual as consisting of those edges not common to an even number of those rings. Associated with each tiling is a *transitivity pqrs* which indicates that there are $p$ kinds of vertex, $q$ kinds of edge, $r$ kinds of face, and $s$ kinds of tile [6]. There are five *regular* nets that have transitivity 1111 [5]. In general we associate smaller numbers in the transitivity with higher regularity.

The *dual* of a tiling is obtained by putting new vertices in the center of the tiles and connecting such vertices by edges passing through common faces (each face of a tiling is common to two tiles) forming an interpenetrating net, so that all rings (faces) of the original structure are linked (catenated) to faces of the dual one and *vice versa*. The dual of a net with transitivity *pqrs* has transitivity *srqp*. It should be apparent that a necessary, but not a sufficient, condition for a net to be dual to an identical net (*self dual*) is that the transitivity be palindromic. Of the regular nets three (those of $SrSi_2$, diamond and primitive cubic) are self dual, and the other two (those of NbO and body-centered cubic) are a dual pair.

When two dual nets are intergrown (interpenetrate) all rings of one net are linked with those of the other and we call the structure *fully catenated*. If two nets that are not duals interpenetrate, they are *partly catenated*.

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## 2. The $CdSO_4$ net

$CdSO_4$ ($HgSO_4$ is isostructural) has a simple structure [7] in which $CdO_4$ and $SO_4$ tetrahedra are linked by sharing corners so that the structure of Cd–O–S links forms a 4-coordinated net (Fig. 1). In its most symmetrical form shown below the net has symmetry $P4_2/mmc$ and there are only two vertices in the unit cell (at 0,0,0 and 0,0,1/2) and the coordination of each vertex is square. The diamond net is the only other 4-coordinated net with just two vertices in the repeat unit.

Fig. 2 shows the net as an assembly of tiles with two hexagonal faces (flat) and two octagonal faces (curved); this is the natural tiling of the net. The tiles are tetrahedra (four faces) with face symbol $[6^2 \cdot 8^2]$.

The $CdSO_4$ net shares with diamond another property—it is self dual. Fig. 3 shows fragments of two interpenetrating nets. The transitivity is 1221 and this is the smallest possible for a self-dual net after that (1111) of the three regular self-dual nets. It is expected therefore that this net will feature prominently in structures based on interpenetrating networks. Indeed it occurs as the net of many metal-organic frameworks, and it is common to find pairs of such nets interpenetrating; for recent examples see e.g. [8–10]. It should be mentioned that 25 years ago A.F. Wells [11], who didn't miss much, noticed that the structure of ice VI is based on two interpenetrating edingtonite nets, and that the underlying topology of edingtonite is that of $CdSO_4$ (although not so identified). The $CdSO_4$ net is also described by Beukemann and Klee [12] who remark of it however "No examples are known".

One might contrast the behavior of the self-dual $CdSO_4$ net with that of a related (and familiar) 4-coordinated net with square coordination—that of NbO. As mentioned above, the dual of the NbO net is the 8-coordinated body-centered cubic net (see e.g. [13]) and, as far as we know, interpenetrating NbO nets have not been observed (we believe that in some instances where this has been claimed, the nets are actually $CdSO_4$ topology).

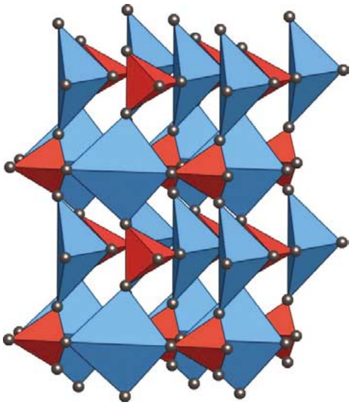

Fig. 1. The structure of $CdSO_4$. $CdO_4$ tetrahedra blue, $SO_4$ tetrahedra red.

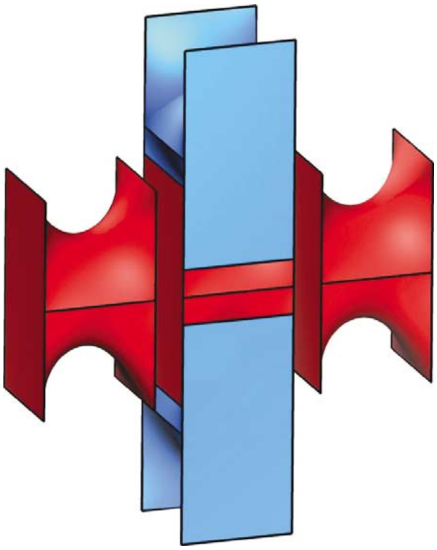

Fig. 2. Tiles of the $CdSO_4$ net. All the tiles are the same but shown in two colors for clarity.

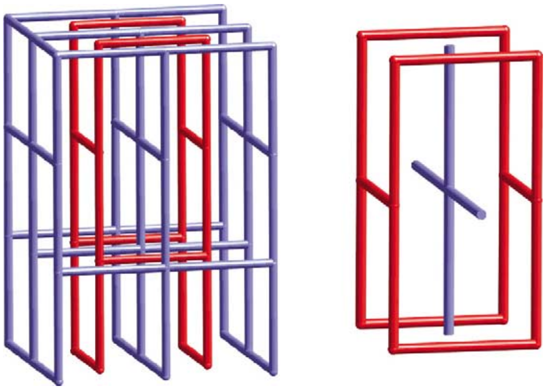

Fig. 3. Left: two interpenetrating $CdSO_4$ nets. Right: the outline of one tile (red) and a vertex and its neighbors (blue) of the interpenetrating net.

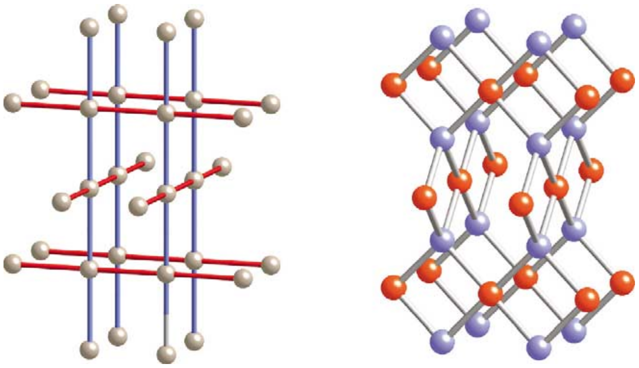

Fig. 4. Left: the $CdSO_4$ net. Right: the cooperite (PtS) net formed from the former by placing vertices in the middle of each link. (S blue sphere in blue link.)

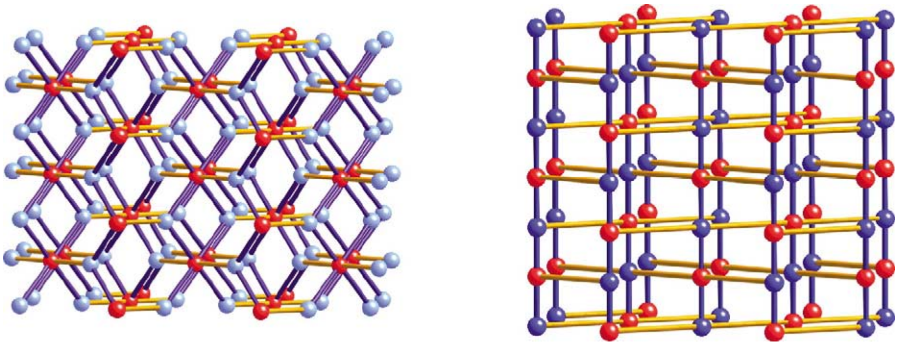

Fig. 5. Left: a fragment of the rutile net. Red spheres are 6-coordinated, blue are three-coordinated. Merging the blue spheres in pairs eliminates the 4-rings and produces the $CdSO_4$ net shown on the right.

## 3. Relationship of the $CdSO_4$ net to those of cooperite and rutile

As the $CdSO_4$ net is one of the two simplest 4-coordinated nets, it is to be expected that other important structures can be simply derived from it. One of the simplest ways of obtaining derived structures [14] is that of placing new vertices in the middle of the edges of the old net; and linking the new vertices to form the *edge net*.[1] In this case one can see easily (Fig. 4) that the derived structure is the cooperite (PtS) net. The PtS net has transitivity 2122 so it is not self dual. However two such nets can interpenetrate with catenation of just the larger rings and interpenetrated cooperite nets are well known (e.g. [15,16]).

The rutile ($TiO_2$) net is also simply related to the $CdSO_4$ net as shown in Fig. 5. Rods of corner sharing quadrangles in the rutile net are condensed by merging pairs of vertices to form straight lines in the $CdSO_4$ net. Interpenetration of rutile nets is well established especially in framework cyanides, see e.g. [17,18]. The transitivity of the rutile structure is 2232; there are two kinds of bonds which penetrate the 6-rings and 8-rings of the interpenetrating structure, leaving the 4-rings uncatenated as in cooperite (Fig. 6).

## 4. The quartz net and its dual

The natural tiles for the quartz net are again tetrahedra $[6^2 \cdot 8^2]$, see Fig. 7, indeed topologically the same as the $CdSO_4$ tiles. However the quartz net has just one kind of edge (link) and the transitivity is 1121 so the quartz structure is not self dual—the dual structure has planar

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[1] Note that in forming the edge net, we link vertices in such a way that the figure around a given vertex is similar to the coordination figure of the vertex. Thus for a vertex in square coordination there are only four links between the four new vertices in the edges incident to the original vertex. In contrast for a vertex in tetrahedral coordination all six possible links are made. Thus the *edge net* we use differs from the *edge graph* of graph theory in which all possible links between new vertices associated with an original vertex are made.

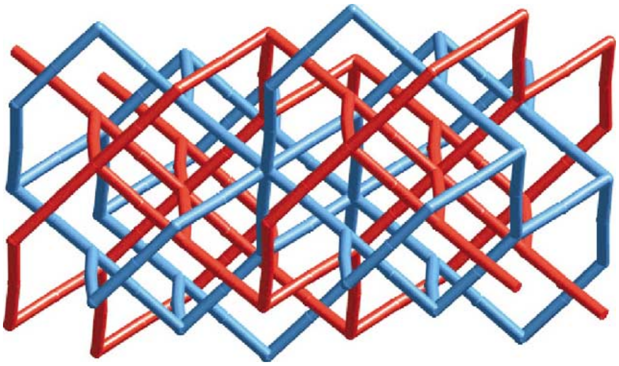

Fig. 6. Two interpenetrating rutile nets. Note the lack of catenation of the 4-rings (see the red net).

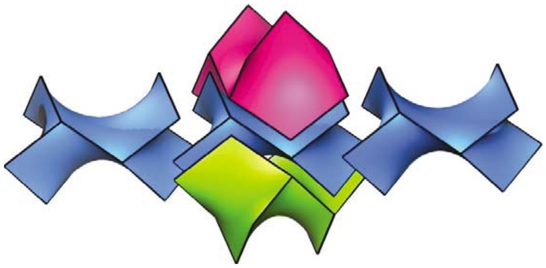

Fig. 7. Natural tiles for the quartz net. The tiles are all the same but shown in different colors for clarity.

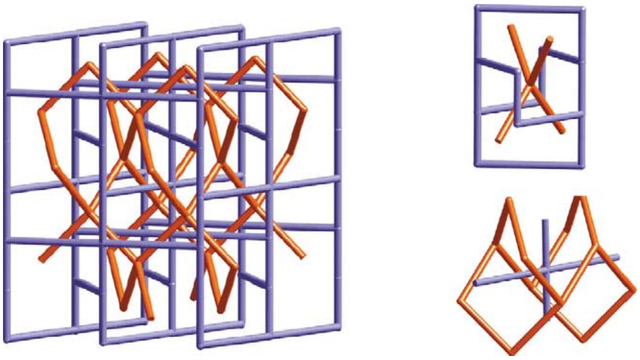

Fig. 8. Left: the quartz net (red) intergrown with its dual (blue). Right top: outline of a quartz dual tile with an interpenetrating fragment of quartz. Right bottom: outline of a quartz tile with an interpenetrating fragment of the dual.

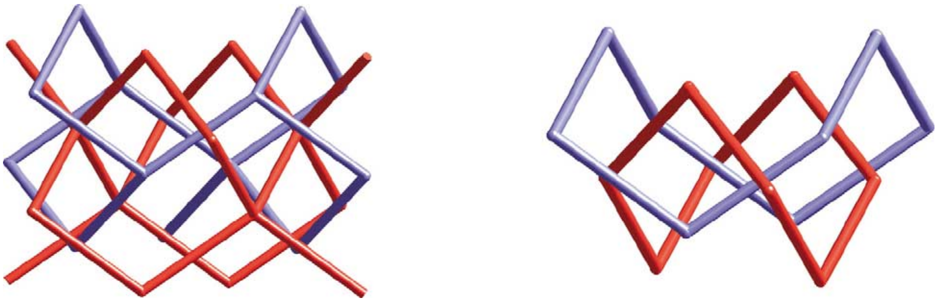

Fig. 9. Left: fragments of two interpenetrating quartz nets. Right: two doubly catenated 8-rings.

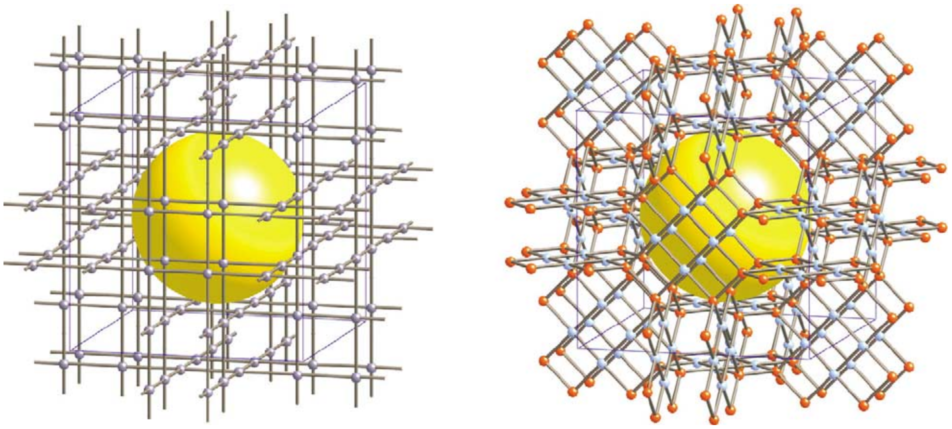

Fig. 10. Left: the net *SSTT*. Right: its edge net. The yellow ball fills an empty cavity in the $Im\bar{3}m$ cell. Coordinates: original net 0.125, 0.125, 0.375; edge net square vertices at 0, 0.125, 0.375, tetrahedral vertices at 0.25, 0.125, 0.375.

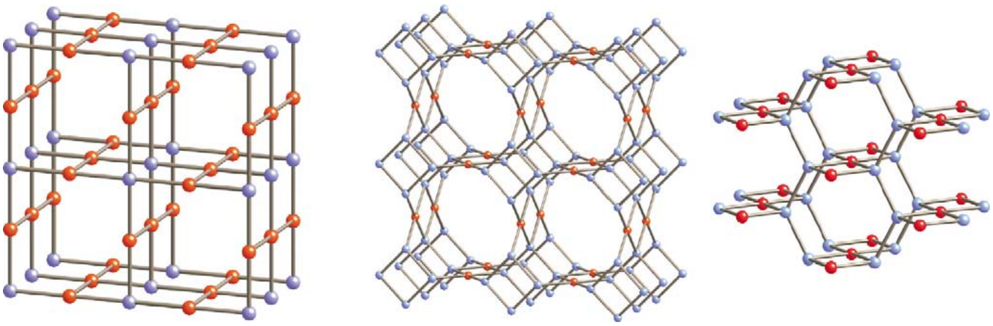

Fig. 11. Left: the MOF-112 net. Center: the edge net of MOF-112. Right: the moganite net.

coordination as shown in Fig. 8—and it is the structure with transitivity 1211 formerly [1,19] called “dense net”. The natural tile of this second structure is a tetrahedron [$7^4$]. The name “dense net” comes from the nature of the coordination sequence, which grows more rapidly with number of coordination shell than that of any other known four-coordinated net [1].

Interestingly the quartz dual net has been observed as a self-interpenetrating framework [20] in a metal-organic structure. The possible positions for vertices of the quartz dual net are position $3a$ or $3b$ of $P6_222$; however for a pair of nets in these positions the edges parallel to **c** overlap, so that in fact two disjoint quartz dual nets cannot intergrow without degradation of symmetry, and will have some rings uncatenated and some multiply catenated as described next for intergrown quartz nets.

The quartz net has also been found interpenetrating in a cyanide structure [21]. As quartz is not self-dual, the nets are not fully catenated, but it is interesting to examine the catenation in two interpenetrating quartz nets more closely. As shown in Fig. 9 the 6-rings are not catenated at all but the 8-rings are doubly catenated; in the jargon [22] a pair of 8-rings have linking number 2.

## 5. Nets related to $CdSO_4$ and cooperite: moganite etc.

There is clearly an infinite family of nets of the $CdSO_4$ type with vertices in square coordination. In the $CdSO_4$ net the links are of two kinds. Those parallel to $c$ that connect vertices whose square coordination figures are at right angles to each other, call these $T$ links, and those perpendicular to $c$ that connect vertices whose coordination figures are coplanar, call these $S$ links. The derived edge nets will have vertices with square coordination in the middle of the original $S$ links and vertices with tetrahedral coordination in the middle of the original $T$ links.

The net with all $S$ links is written *SSSS* and is the plane net $4^4$. The net *TTTT* is the NbO net and the corresponding edge net is that of sodalite (see e.g. [11,14,19]). $CdSO_4$ is *STST* (i.e. the links alternating $S$ and $T$ around the vertex) and the corresponding edge net is cooperite (Fig. 4).

It is an interesting exercise to systematically enumerate possibilities, but we only give two examples here. The combination *SSTT* produces the beautiful open cubic structure shown in Fig. 10 with 24 vertices in the repeat unit (contrast 2 for *STST*). The derived edge net, also shown in the figure, contains equal numbers of square and tetrahedrally-coordinated vertices with squares of square vertices linked to hexagons of tetrahedral vertices, and hence three kinds of link (edge). We believe the cooperite structure is the *only* one in which square and tetrahedral vertices are linked by just one kind of link.

An interesting case was found recently in the net of MOF-112 [23] which is constructed of linked square copper carboxylate “paddle wheels” by linkers that can join the squares in a parallel fashion $(S)$ or twisted by 90° $(T)$. The vertices of the net (Fig. 11) are $TTTT + 2STST$ and there are only three vertices in the repeat unit. The edge net (Fig. 11) has vertices with square and tetrahedral coordination in the ratio 1:2. In this connection it is appropriate to call attention to another simple net with only three vertices in the repeat unit that also has square and tetrahedral vertices in the ratio 1:2 [14,19]. This is the net (also shown in Fig. 11) of the moganite form of silica; it is also found in expanded framework structures such as a form of $Cd(CN)_2$ [24].

## 6. Concluding remarks

The basic four-coordinated nets we have discussed here—those of diamond, $CdSO_4$, quartz, quartz dual—are carried by tiles that are tetrahedral cages; respectively $[6^4]$, $[6^2 \cdot 8^2]$, $[6^2 \cdot 8^2]$, $[7^4]$. Accordingly their duals are also four-coordinated nets. For the design of possible composite materials with interpenetrating nets, it would be interesting to know what other, if any, four-connected nets also have his property.

We find it remarkable that the $CdSO_4$ and quartz dual nets, which are among the simplest of all 4-coordinated nets, were generally unknown just over a decade ago. They are characterized by having bonds running in straight lines in respectively two and three directions normal to the principal axis of symmetry. Accordingly they have the same symmetry ($P4_2/mmc$ and $P6_222$) as cylinder packings [25] based on the same principle. One of us (M. O’K.) would like to acknowledge a personal debt owed to Sten Andersson who introduced him to this and many other related, and beautiful, topics in descriptive geometry in 1976 and later.

We should also remark that self-dual nets occur as the labyrinth systems of balance minimal surfaces that divide space into two equal components. These are important in several areas of crystal chemistry and elsewhere, as Sten Andersson and S.T. Hyde in particular have emphasized [26,27]; the three regular self-dual nets are familiar in this regard as the labyrinths of the $G$, $D$, and $P$ surfaces, and interpenetrating $CdSO_4$ nets form the labyrinths of the *CLP* surface [26] which is predicted to be of some importance in biological structures [28] (see the contribution of Terasaki, Larsson and Larsson to this issue).

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