The Geometrical Basis of Crystal Chemistry.
XII. Review of Structures Based on Three-Dimensional 3-Connected Nets

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For a number of three-dimensional 3-connected nets the symmetry of the most symmetrical configuration of the net is compared with the space group(s) of the actual crystal structure(s) based on the net. The close correspondence found in most cases indicates that in general a net describes not only the topology but also the symmetry of a structure.

Introduction

In previous papers of this series a number of three-dimensional 3-, (3,4)-, and 4-connected nets have been derived. The earlier work, together with much unpublished material, has recently been summarized in a monograph (Wells, 1976). In this paper we review the structures based on three-dimensional 3-connected nets and compare their symmetries with those of the most symmetrical configurations of the nets on which they are based. The justification for describing certain structures in terms of such nets is not simply that this provides a convenient way of describing the structures. The *only* way in which the basic topology of such structures can be correctly and succinctly described is to specify the three-dimensional nets on which they are based. Moreover, the description of a structure in this way ensures that it can be recognized even if referred to different axes (Strong, Wells & Kaplow, 1971). This final stage in the description of a structure is rarely carried out by X-ray crystallographers; a notable exception is the description of the structure of high-SiP_2O_7 in terms of its basic net, the (4,6)-connected pyrite net (Tillmanns, Gebert & Baur, 1973). Polymorphs are conveniently characterized by specifying their nets provided these are topologically distinct, as is true of the cubic and the two monoclinic forms of SiP_2O_7. Perhaps more important is the fact that the correct description of the topology of a structure of the type we are considering is a necessary preliminary to attempting to understand why the particular structure is adopted.

Nets are described in terms of their polygonal circuits (*n*-gons) and connectedness (*p*), and we shall be concerned here for the most part with nets having the special property that the shortest circuit starting from any point and including *any two* of the links meeting at the point is an *n*-gon. Such a net is described as a *uniform net*. The known uniform three-dimensional 3-connected nets now number thirty: one uniform (12,3), seven uniform (10,3), three uniform (9,3), fifteen uniform (8,3), and four uniform (7,3) nets. They include all the nets discussed later except $6 . 10^2$;

this symbol indicates that the smallest polygons meeting at each point are one 6-gon and two 10-gons. The uniform nets are derived as topological entities (*n*,*p*), that is, the symbol gives only the number (*n*) of links in each (shortest) circuit and the number (*p*) of links meeting at each point. In contrast to the unique two-dimensional 3-connected net (6,3) the uniform three-dimensional 3-connected nets are in general not adequately described by the symbol (*n*,*p*); there are, for example, seven known (10,3) nets. It is usually sufficient to specify also the following purely topological properties of a net, that is, properties independent of the particular geometrical configuration of the net: Z_t, the number of points in the smallest (topological) unit cell, $^n x$, the number of *n*-gon circuits to which each point belongs, and $^n y$, the number of *n*-gon circuits to which each link belongs. These data for the seven uniform (10,3) nets are listed in Table 1. It may happen that even the values of Z_t, $^n x$, and $^n y$ are not sufficient to define a net uniquely; for example, they do not distinguish (8,3)-*a* from (8,3)-*b* (two of the nets listed in Table 2). In such cases it would be necessary to determine the values of *x* and *y* relating to larger circuits.

So far we have considered only the topology of a

Table 1. *Topological data for uniform* (10,3) *nets*

Z_t number of points in smallest cell (topological), ^{10}x number of 10-gon circuits to which each point belongs, ^{10}y number of 10-gon circuits to which each link belongs.

Net	Z_t	^{10}x	^{10}y	$^{10}y_{mean}$
(10,3)-*a*	4	15	10	(30/3)
b	4	10	8,6,6	20/3
c	6	5	4,3,3	10/3
d	8	10	8,6,6	20/3
e	12	9,11	8,6,6	20/3
f	16	10	8,6,6	20/3
g	20	12	8	(8)

Note: The net (*e*) has equal numbers of two kinds of non-equivalent point, and the nets (*b*)–(*f*) inclusive have two kinds of non-equivalent link, one third of one kind and two thirds of the other. Note that the number of links per cell is equal to $3Z_t/2$ and that the numbers given in the ^{10}y column refer to the three links meeting at each point.

net. Before discussing the metrical features (geometry) of nets it is pertinent to examine the types of crystal structure based on them.

Structures based on three-dimensional 3-connected nets

The simplest types of structural unit which might be expected to form periodic three-dimensional 3-connected nets (or any other kind of 3-connected system) are shown in Fig. 1. For coordination groups AX_3, AX_4 and AX_6 in (b)–(d) the compositions are A_2X_3, A_2X_5 and AX_3 respectively. Correspondence between the symmetry of a structure and that of the most symmetrical configuration of a net might be expected to be closest in case (a) and progressively less close in (b), (c) or (e); no examples of (d) are known. In describing the structure of B_2O_3 as based on the net $(10,3)$–c we suppose that we disregard the (2-connected) O atoms which connect the B atoms, leaving a link connecting each pair of these atoms. Similarly, in describing the structure of one form of P_2O_5 as
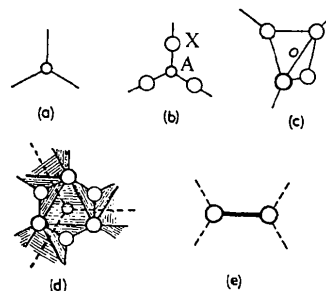

Fig. 1. Structural units in 3-connected systems.

based on the net $(10,3)$–b we disregard all the O atoms, some of which are bonded to only one P atom while the remainder link the P atoms into a three-dimensional 3-connected net. In replacing
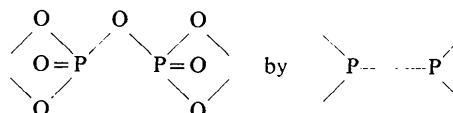

Table 2. *Structures based on three-dimensional 3-connected nets*

Net	Most symmetrical configuration			Compound	Space group	Reference[d]
	Space group	Position	$c:a$			
$(10,3)$-a $(120°)$	$I4_132$	$8(a)$		$SrSi_2$	$P4_132$	1
				$CsBe_2F_5$	$P4_132$	2
$(10,3)$-a $(90°)$	$I2_13$			H_2O_2	$P4_12_12$	3
				α-$Hg_3S_2Cl_2$	$I2_13$	4
$(10,3)$-b $(120°)$	$I4_1/amd$	$8(e)$ $(0,0,\frac{1}{12})$	$2\sqrt3$	$Sn_2F_3Cl^a$	$P2_13$	5,6
				α-$ThSi_2$	$I4_1/amd$	7
				P_2O_5	$Fdd2$	8
				(Zn_2Cl_5) (H_5O_2)	$Fdd2$	9
				$(CH_3)_2S(NH)_2^a$	$Fdd2$	10
$(10,3)$-b $(90°)$	$C2/c$			[GeS_2	$Fdd2$	11]*
$(10,3)$-c	$P3_112$	$6(c)$ $(\frac{1}{3},\frac{1}{6},\frac{1}{3})$	$3\sqrt3/2$	$La_2Be_2O_5$	$C2/c$	12
$(10,3)$-d	$Pnna$	$8(e)$		B_2O_3	$P3_1$	13
				α-Resorcinol }		14
$(8,3)$-a	$P6_222$	$6(i)$ $(\frac{2}{3},\frac{4}{3},0)$	$3\sqrt2/5$	β-Resorcinol }	$Pn2_1a$	15
				Caryophyllene		
				chlorohydrin	$P3_1$	16
$(8,3)$-b	$R\bar3m$	$18(f)^c$ $(\frac{2}{3},0,0)$	$\sqrt6/5$	$C_6H_4\{Si(CH_3)_2OH\}_2$	$P\bar1$	17
$6 \cdot 10^2$	$R\bar3m$	$18(f)^{b,c}$		$N_4(CH_2)_6 \cdot 6H_2O$	$R3m$	18
				β-Quinol	$R\bar3, R3$	19

(a) These two examples of the nets were noted after the paper was written and had been submitted for publication, and for that reason the structures are not discussed in the text. In Sn_2F_3Cl each Sn atom forms three bonds to bridging F atoms. Another study (Donaldson, 1976) shows that the symmetry of Sn_2F_3Cl is only orthorhombic (space group $P2_12_12_1$) but markedly pseudocubic, $a=b=c=7.880$ Å. The dimethyl sulphone diimine structure is similar to that of hydrogen peroxide (though based on a different net) in that each N atom is hydrogen-bonded to N atoms of two other molecules:

$$H\cdots N-S(CH_3)_2-N\cdots H$$
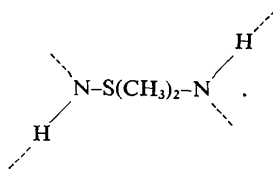
The author hopes to comment on the structures of the tin and mercury compounds listed in Table 2 in a later paper. (b) No unique configuration is possible with all links of equal length and all interbond angles equal to 120°. (c) Hexagonal setting. (d) Key to references: (1) Janson, Schäfer & Weiss (1970), Pringle (1972). (2) Le Fur & Aléonard (1972). (3) Abrahams, Collin & Lipscomb (1951). (4) Frueh & Gray (1968). (5) Bergerhoff & Goost (1974). (6) Donaldson (1976). (7) Brauer & Mitius (1942). (8) de Decker (1941). (9) Follner (1970). (10) Prince (1975). (11) Zachariasen (1936). (12) Harris & Yakel (1968). (13) Strong & Kaplow (1968). (14) Robertson (1936). (15) Robertson & Ubbelohde (1938). (16) Rogers & Mazhar-ul-Haque (1963). (17) Alexander, Northolt & Engmann (1967). (18) Mak (1965). (19) Palin & Powell (1947).

* *Note added in proof*: A redetermination (Dittmar & Schäfer, 1976) shows that low-GeS_2 is actually monoclinic (space group Pc), the structure being essentially the same as that of Zachariasen (1936).

we are taking no account of the oxygen bond angles or of the packing of the O atoms, though both factors are important in determining the atomic arrangement in the crystal. The representation of the structure of a crystalline dihydroxy compound such as H_2O_2 or *m*-dihydroxybenzene (resorcinol), $OH.C_6H_4.OH$, as a 3-connected net implies regarding the hydrogen-bonded molecule as a pair of 3-connected points as in Fig. 1(*e*). In the resulting three-dimensional net one third of the links represent the axes of the molecules and the remainder O–H···O bonds. In these two nets the approximate lengths of the two kinds of link are:

	O–O	O–H···O
H_2O_2	1·5 Å ⎫	
$HO.C_6H_4.OH$	5·5 ⎭	2·8 Å.

Moreover, the representation of the crystal structure of resorcinol in this way implies neglecting the benzene ring which is responsible for most of the volume of the molecule.

Evidently, in view of the above facts, it is to be expected that if the structures of two compounds of different chemical types are based on the same net the geometrical configurations of the basic net as found in the actual structures (for example, by joining together the P atoms in P_2O_5 or the Si atoms in $ThSi_2$) may be very different and perhaps difficult to recognize as forms of the same net [in this case (10,3)-*b*]. It is therefore essential to know the most symmetrical configuration of a given net; this is the standard reference configuration with which to compare the various distorted configurations found in actual crystal structures. We shall see later that it may be convenient to recognize more than one standard configuration of certain nets.

Symmetry of structure and net compared

In view of the simplifications made when describing a structure as based on a particular net it might appear that the most symmetrical form of a net is a mathematical abstraction of somewhat dubious interest, bearing little relation to the actual crystal structure. However, Table 2 shows that in fact there is usually a close relation between the symmetries of actual crystal structures and those of the most symmetrical configurations of the nets on which they are based. The most symmetrical arrangement of three bonds meeting at a point is that with all interbond angles 120°, and if a net can be constructed in three dimensions with all links of equal length and all bond angles 120° this is the configuration whose space group is listed in column 2. Such a configuration is possible for three (10,3), two (9,3), and four (8,3) nets, and this special class includes all the nets in Table 2 except (10,3)-*d* and 6 . 10².

Both of the nets (10,3)-*a* and (10,3)-*b* have four points in the smallest (topological) unit cell and eight in the unit cells of their most symmetrical configurations (equal links and 120° bond angles). These configurations have respectively cubic and tetragonal symmetry (Fig. 2). A second special configuration is recognized for these nets, namely, one with equal links and bond angles of 90°, because it is found that there are crystal structures corresponding to both forms of each net. These special configurations may be derived from a portion of the primitive cubic lattice containing eight points by removing one half of the links. This operation may be carried out in many ways, to leave isolated cubes, chains, layers or three-dimensional nets. Of the numerous possibilities the two shown in Fig. 3 correspond to (10,3)-*a* (90°) and (10,3)-*b* (90°). In order to assign space groups to these configurations it is necessary to indicate the positions of the links, since the points themselves form a simple cubic lattice in all diagrams of this kind. This is done by placing (2-connected) points at the mid-points of the links; these would be the positions of the X atoms in a compound A_2X_3 based on this net or of the shared X atoms in a framework of composition A_2X_5 formed from tetrahedral AX_4 groups sharing three vertices. For (10,3)-*a* (90°) such points are the position 12(*b*) of $I2_13$ for the special value $x=\frac{1}{2}$. The structure of α-$Hg_3S_2Cl_2$ is based on this net with S atoms in 8(*a*) and Hg atoms in 12(*b*) of this space group.

The unit cell of (10,3)-*b* (90°), Fig. 3(*b*), is a cube but the space group, determined in the above way, is $C2/c$, which is that of $La_2Be_2O_5$. The unit cell approximates to a cube: $a=7.54$, $b=7.35$, $c=7.44$ Å, $\beta=91°33'$, and the Be atoms occupy the positions 8(*f*), (*xyz*) etc., with $x=0.47$, $y=0.22$, $z=0.53$. These coor-
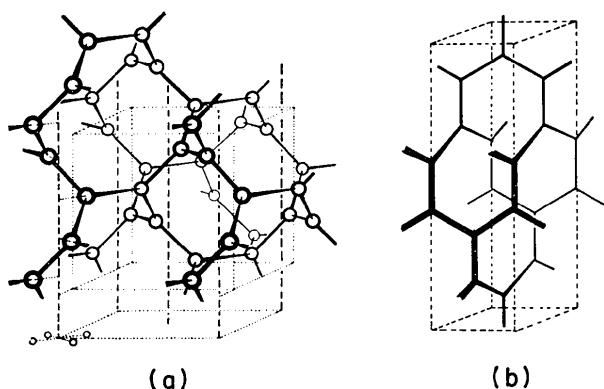

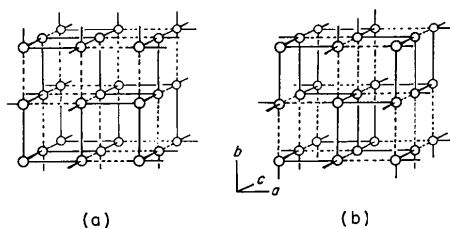Fig. 2. The nets (10,3)-*a* (120°) and (10,3)-*b* (120°).

Fig. 3. The nets (10,3)-*a* (90°) and (10,3)-*b* (90°).

dinates are close to the values $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{2}$, and the eight Be atoms lie approximately at the points of a primitive cubic lattice with cell edge $a/2$ ($=b/2=c/2$). The three sets of (four) shared O atoms occupy positions $4(d)$, $4(e)$ $(0,y,\frac{1}{4})$ with $y=\frac{1}{4}$, and $4(b)$, so that they have coordinates respectively $(\frac{1}{4},\frac{1}{4},\frac{1}{2})$, $(0,\frac{1}{4},\frac{1}{4})$, and $(0,\frac{1}{2},0)$, which are the midpoints of one half of the 'links'. The arrangement of the Be atoms therefore corresponds very closely to that of the circles in Fig. 3(b) and the shared O atoms are at the midpoints of the links drawn with full lines. This structure based on the net (10,3)-b (90°) has room for eight La in the octants of the pseudo-cubic cell which contains eight Be, and it is therefore suitable for a compound $A_2B_2X_5$, in contrast to the structure of $CsBe_2F_5$ based on (10,3)-a (120°) which accommodates only one Cs for every two Be in the framework. We now discuss the remaining structures of Table 2 which are less symmetrical than the most symmetrical forms of the underlying nets.

In $SrSi_2$ and $CsBe_2F_5$ the unit cell contains eight atoms (Si or Be) corresponding to the eight 3-connected points of (10,3)-a. In $SrSi_2$ the net is formed from Si atoms which are directly bonded together, with Sr atoms in the interstices, while in $CsBe_2F_5$ the framework is formed from BeF_4 tetrahedra sharing three vertices (F atoms). Each Be is connected through F atoms to three others, and the Cs^+ ions occupy the interstices. The similarity between the structures is evident from Fig. 4. The space group $I4_132$ is not possible for these crystals because occupation of $8(a)$ by the atoms forming the net would require a fourfold position for Sr or Cs respectively and there is no fourfold position in $I4_132$. (The higher space group would also imply coplanar Si bonds – see later.) A similar problem does not arise for α-$ThSi_2$ because $I4_1/amd$ has the required fourfold position.

In crystalline H_2O_2 the 4_1 helices are formed by the hydrogen bonds, which here constitute two thirds of the links of the basic net. Since their length (2·78 Å) is so much greater than that of the remaining links, which are the intramolecular O–O bonds of length 1·47 Å, the net is very distorted from the ideal configuration. The 4_1 axes are retained but the symmetry drops to tetragonal and the space group is $P4_12_12$. The net is so distorted that it is virtually 5-connected, for each O atom also has two other O atom neighbours at 2·90 Å.

The net (10,3)-b, Fig. 2(b), is somewhat more complex because the 120° configuration can be 'sheared', a process involving rotations about those links which are parallel to the tetragonal c axis. The fully extended tetragonal form of the net represents the arrangement of the Si atoms in α-$ThSi_2$. In sheared forms the 8-point body-centred tetragonal cell becomes non-orthogonal but the sheared net may be referred to an all-face-centred orthogonal cell containing 16 points. These are alternative cells for the space group $Fddd$ (Fig. 5). This relation is similar to that between the

f.c.cubic and b.c.tetragonal cells of diamond. We may refer cubic diamond to a b.c.tetragonal cell containing four atoms in $4(a)$ of $I4_1/amd$ and conversely we may refer the net (10,3)-b to a 16-point f.c. cell with space group $F4_1/ddm$ which is the alternative setting of the same space group. In both cases the most symmetrical orthorhombic sub-group is $Fddd$. In fact we find that one form of P_2O_5 and also (Zn_2Cl_5) (H_5O_2) both have the space group $Fdd2$ with P or Zn occupying the general position $16(b)$. We have also included GeS_2 in Table 2. Its crystal structure is a three-dimensional assembly of GeS_4 tetrahedra of which each vertex (S atom) is common to two tetrahedra. The Ge atoms are situated at the points of a 4-connected net, this net being formed by joining together the midpoints of adjacent links of (10,3)-b so as to form triangles around the points of the original 3-connected net. In this case also the space group is $Fdd2$, but whereas P_2O_5 and (Zn_2Cl_5) (H_5O_2) have 16 3-connected points (P or Zn) in the unit cell, GeS_2 has $Z=24$ since here the Ge atoms are situated at the mid-points of the links of the 3-connected net. The relation of these structures to (10,3)-b (120°) is also seen from the cell dimensions of these crystals. For the tetragonal configuration of (10,3)-b, $c:a=2\sqrt{3}=3\cdot46$, and $\beta=90°$. The corresponding figures for the b.c. monoclinic $(Z=8)$ cells of the other compounds are:

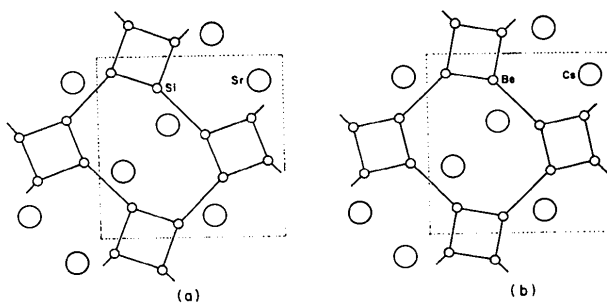|	a $(=b)$	c	β (approximate)	$c:a$
P_2O_5	4·85 Å	16·3 Å	114°	3·36
(Zn_2Cl_5) (H_5O_2)	6·43	22·90	92	3·56
GeS_2	6·77	22·34	119	3·30 .

Fig. 4. Projections on (001) of (a) the Sr and Si atoms of $SrSi_2$, (b) the Cs and Be atoms of $CsBe_2F_5$.
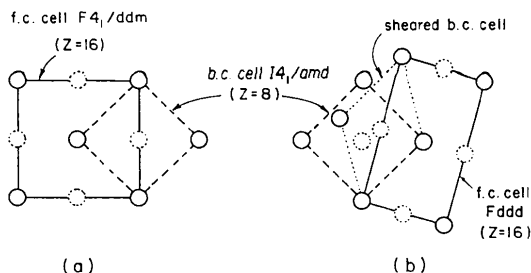

Fig. 5. (a) Relation between the F and I cells of (10,3)-b projected along c axes; the dotted circles represent points at height $c/2$ above the paper. (b) Relation between the b.c. cell of 'sheared' version of (10,3)-b (dotted lines) and the orthorhombic F cell (full lines).

The reason for the adoption of the less symmetrical space group is as follows. In *Fddd* the 16 tetrahedrally coordinated atoms (P or Zn) would have to occupy two sets of eightfold positions (point symmetry 222) or one of the sixteenfold positions (c)–(g). Of the latter, (c) and (d) are excluded because the point symmetry is $\bar{1}$ while in (e), (f) or (g) or in the eightfold positions the tetrahedra would lie on twofold axes, which is not possible if they are to share three vertices. In *Fdd2* the tetrahedral groups can occupy the general sixteenfold position. This simple argument does not apply to GeS_2. In *Fddd*, with 24 Ge in the cell, it would be necessary to utilize an eightfold position, and presumably the occupation of one of these special positions (with no variable parameters) would impose too great a restriction on the packing of the atoms.

A feature of several other structures (B_2O_3, α- and β-resorcinol and caryophyllene chlorohydrin) is that the symmetry is lower than that of the most symmetrical configuration of the net by the absence of one or more sets of twofold axes. At this time, without detailed studies of these structures, we can only suggest that, as in the case of GeS_2, the additional symmetry would not be consistent with satisfactory packing in the crystals. Just as the 4_1 screw axes characteristic of $(10,3)$-a
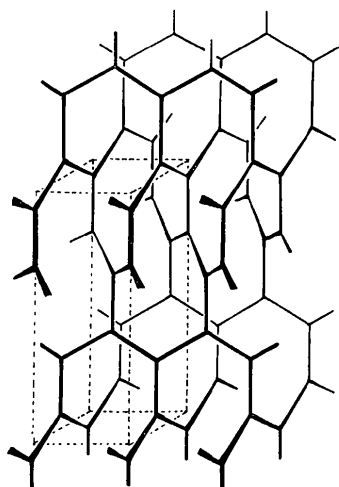

Fig. 6. The net $(10,3)$-c. [The unit cell is not that of *International Tables* but has its origin at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$.]
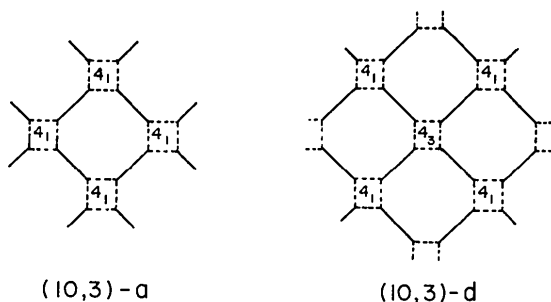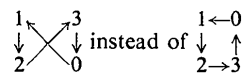

(10,3) - a   (10,3)-d

Fig. 7. Projections of nets $(10,3)$-a and $(10,3)$-d along the fourfold screw axes.

$(120°)$ are retained in the less symmetrical structure of H_2O_2, so the essential features of the net are retained in the structures noted above.

The net $(10,3)$-c (Fig. 6) is the trigonal (or hexagonal) analog of the (tetragonal) net $(10,3)$-b $(120°)$. The characteristic sub-unit in both nets is the planar zigzag chain. Repetition of such a chain by 2_1 axes in the plane of the zigzag gives the planar 6-gon net. In $(10,3)$-b the chain directions are the a and b axes, and the chains are repeated around 4_1 axes which are parallel to the c axis. In $(10,3)$-c the chains are parallel to three equivalent directions perpendicular to c and they are repeated by the operation of 3_1 axes. Owing to the special values of the coordinates, namely, $x = \frac{1}{3}$, $y = \frac{1}{6}$, and $z = \frac{1}{9}$ in the general position $6(c)$ of $P3_112$, there are also 6_4 screw axes. [In the earlier description of this net (Wells, 1972) the unnecessarily complicated coordinates $x = \frac{1}{6}$, $y = \frac{5}{6}$ and $z = \frac{1}{18}$ were given for $6(c)$ in $P3_212$.] It can be shown that there is no three-dimensional net analogous to $(10,3)$-b and $(10,3)$-c generated from planar zigzag chains by the operation of 6_1 axes (Wells, 1976).

The net $(10,3)$-d cannot be constructed with all links of equal length and all interbond angles $120°$, though it can be built with all links equal in length and with exact 4_1 and 4_3 helices. This and other configurations are derivable from the general (eightfold) position in *Pnna* with appropriate values of x, y, and z. This net may be derived in two ways. It is the second member of a family of nets which project as the planar $4:8$ net. The first member is $(10,3)$-a in which all the fourfold helices are of the same chirality, while in $(10,3)$-d the helices which are directly connected are of opposite chirality (Fig. 7). Alternatively we may use the operation

$$\begin{matrix} 1 & & 3 \\ \downarrow & \times & \downarrow \\ 2 & & 0 \end{matrix} \quad \text{instead of} \quad \begin{matrix} 1 \leftarrow 0 \\ \downarrow \quad \uparrow \\ 2 \rightarrow 3 \end{matrix}$$

described in an earlier paper as a '4_{12} axis' (Wells, 1956), in which case $(10,3)$-d is the second member of the family which starts with $(10,3)$-b (Fig. 8). These two ways of deriving this net correspond to the use of the net in the two polymorphs of resorcinol. In the α form the hydrogen bonds form the fourfold helices, the broken lines in Fig. 7, while in the β form they correspond to the '4_{12} axes'. These configurations of $(10,3)$-d afford a unique example of the use of the same net in two quite different ways by the same compound with the same space group. The space group $Pn2_1a$ has no diad axes, whereas there are two sets of diads in *Pnna* (full symbol $P2/n2_1/n2/a$). In the latter space group molecules of m-$C_6H_4(OH)_2$ could not be placed in fourfold positions $4(a)$ or $4(b)$ with point symmetry $\bar{1}$ and would have to be situated in $4(c)$ or $4(d)$ on diad axes. This is presumably not consistent with efficient packing of the benzene rings and simultaneously the formation of chains of hydrogen bonds.

We are aware of only one structure based on each of the nets (8,3)-a and (8,3)-b, the relation between which can be seen from the projections of Fig. 9. The unsymmetrical molecule of caryophyllene chlorohydrin, $C_{14}H_{21}Cl(OH)_2$, contains two OH groups, and the basic topology of the crystal structure is determined by its behavior as a dihydroxy compound. The hydrogen bonds form threefold helices all of the same chirality, and the whole structure has trigonal symmetry $P3_1$ (Fig. 10). In crystalline $HO(CH_3)_2SiC_6H_4Si(CH_3)_2OH$ the trigonal symmetry $R\bar{3}m$ of the most symmetrical configuration of the net (8,3)-b is not retained, and the structure has only triclinic symmetry (with $Z=3$, to give six OH in the unit cell). However, the helical arrangement of the hydrogen bonds is evident in the projection of Fig. 11, and in the description of the structure it is noted that 'the geometry about the hydrogen-bond axes shows a distinct tendency in the direction of 3_1 helical symmetry'. The molecules are situated at three of the four symmetry centres in the unit cell so that alternate helices are of opposite chirality as required in the net (8,3)-b.

The most symmetrical configurations of the net $6 . 10^2$, one of which is illustrated in Fig. 12, have the symmetry of the space group $R\bar{3}m$ with $Z=6$ for the rhombohedral cell or 18 for the hexagonal cell. There is no configuration with all links equal in length and all interbond angles equal to 120°, but the hexagons are planar (and regular) and all links of equal length for appropriate ranges of values of $c:a$ and of x in position 18(f) (hexagonal cell) or puckered in a range of configurations having three equal coplanar links

meeting at each point (for details see Wells, 1976). The structures based on this net have lower symmetry than $R\bar{3}m$. In the hexahydrate of $N_4(CH_2)_6$ the hexamethylenetetramine molecules are situated in the interstices of the net formed by the hydrogen-bonded water molecules, and the most symmetrical space group compatible with the point symmetry ($3m$) of the $N_4(CH_2)_6$ molecule is $R3m$. In 'β-quinol' there are two
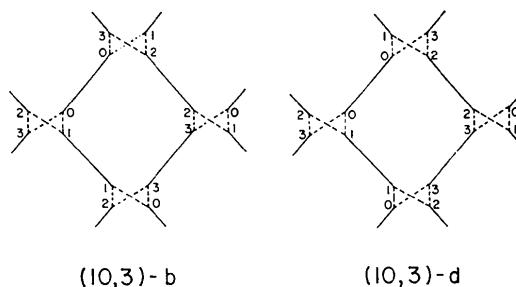

(10,3)- b   (10,3)-d

Fig. 8. Projections of the nets (10,3)-b and (10,3)-d along the 4_{12} axes.
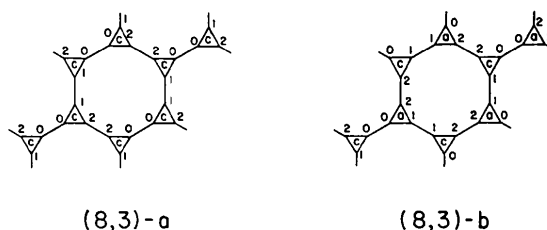

(8,3)-a   (8,3)-b

Fig. 9. Projections of the 3-connected nets (8,3)-a and (8,3)-b.
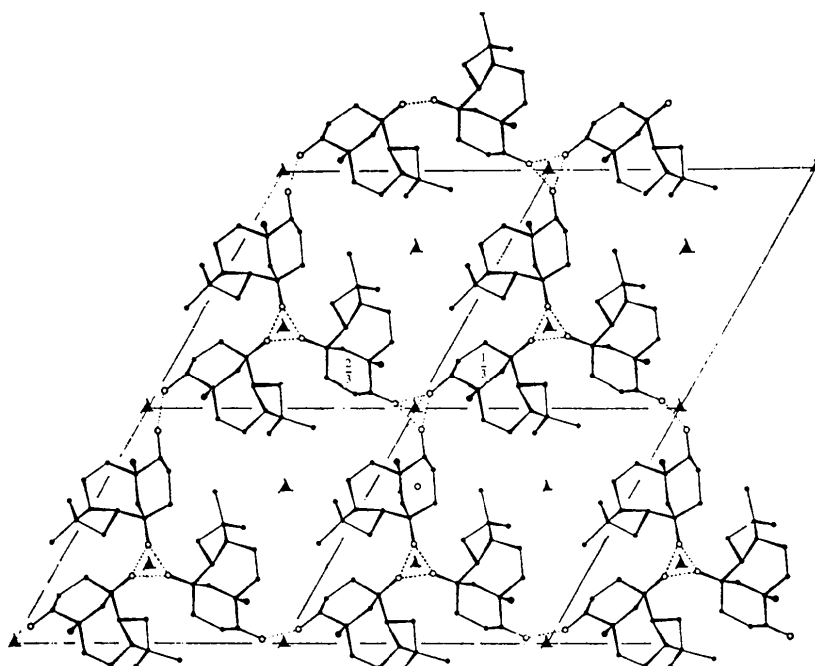

Fig. 10. Projection of the structure of caryophyllene chlorohydrin.

identical interpenetrating nets. Here the vertical symmetry planes are absent because of the relative orientations of the benzene rings, which are situated along the links of the framework. As in the former structure there are molecules of a second compound X (or in the argon compound, atoms of argon) in the interstices of the framework, and the composition is approximately $C_6H_4(OH)_2.\frac{1}{3}X$. In each structure the interstitial molecule (atom) is situated at the origin of the rhombohedral cell, where the point symmetry corresponds to the space group symbol. In $C_6H_4(OH)_2.\frac{1}{3}SO_2$ the SO_2 molecule becomes effectively centrosymmetric by rotation and the space group is $R\bar{3}$, but in $C_6H_4(OH)_2.\frac{1}{3}CH_3OH$ the methanol molecule apparently cannot rotate about a horizontal axis and the space group is $R3$.

Discussion

One of the reasons for studying crystal structures is to understand why particular structures are adopted by the various elements and compounds. For the compounds under discussion we might enquire (a) why a
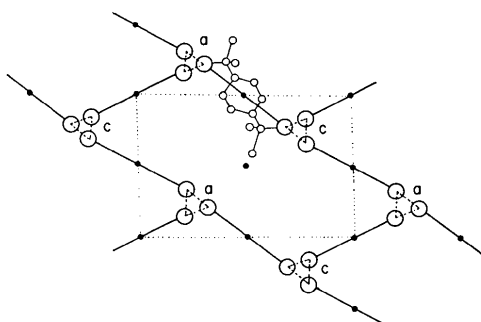
Fig. 11. Projection of the structure of $C_6H_4[Si(CH_3)_2OH]_2$. For all molecules except one only the HO–OH axis is shown. The letters c and a indicate clockwise and anticlockwise helices. The small black circles indicate symmetry centres and the larger open circles OH groups.
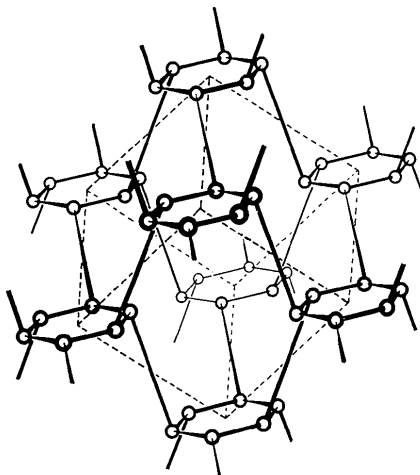
Fig. 12. The 3-connected net 6.10^2.

structure is based on a 3-connected net, (b) why this should be a three-dimensional net, (c) why one particular net is chosen in preference to others, and (d) why in some cases the symmetry of the structure is lower than that of the most symmetrical configuration of the net. These questions are inter-related, as we shall show for certain silicides. We may distinguish (a) as essentially a chemical problem, a matter of the electronic structures of atoms and of their interactions, and this is not the place to discuss the reasons why the units of Fig. 1 form 3-connected nets. We shall comment briefly here on (b) and (c); (d) has already been discussed.

The second question, (b), is perhaps the most difficult one to answer. For structural units which are to be linked to three others the resulting 3-connected system could be finite or infinite in one, two, or three dimensions. As regards freedom to adapt to the bonding requirements of the atoms a three-dimensional framework would appear to be the least favorable type of structure. A chain or layer structure would seem to be more adaptable and a structure built of finite units still more so. Phosphorus pentoxide is remarkable for crystallizing with structures of three of the four main types, namely, finite (P_4O_{10} molecules), layer, and three-dimensional framework. However, almost all compounds $A_mB_2X_5$ have layer structures: $M_2Si_2O_5$ (M = Li, Na, K, Rb, Ag, Tl), $BaSi_2O_5$, MBe_2F_5 (M = Rb, Cs, Tl and probably K and NH_4). Only $La_2Be_2O_5$ and one polymorph of $CsBe_2F_5$ are at present known to form structures based on three-dimensional nets. The 6-gon layers in the silicates buckle to various degrees to accommodate a range of cations (for a review see Liebau, 1968). Tetrahedral Si_4^{4-} ions can pack with cations ranging in size from Na^+ to Cs^+ (in NaSi etc.) or with one half the number of Ba^{2+} ions in $BaSi_2$. In fact the only sizeable group of compounds with structures based on a three-dimensional net are the 4f and 5f disilicides with the $ThSi_2$ structure, and three of these compounds also crystallize with the AlB_2 structure:

|	M in MSi_2
$ThSi_2$ structure:	Th, U, Pu; La − Ho
AlB_2 structure:	Th, U, Pu; Er, Tm, Yb, Lu .

Elementary silicon does not have a graphitic form but three coplanar bonds are formed by Si in the closely related AlB_2 and $ThSi_2$ structures. The 12-coordination of the metal atom is extremely similar in these two structures, which must have very similar energies; there are no diborides with the $ThSi_2$ structure.

The next question, (c), concerns the choice of a particular net. Of the structures listed in Table 2 most are based on the simplest and most symmetrical three-dimensional nets. The types of compound with structures based on particular nets and the distortions (if any) from the most symmetrical configurations suggest that the atomic (electronic) interactions lead to

some preferred bond arrangement which in turn leads to a particular type of sub-unit of structure. For example, the 'graphitic' behavior of Si is satisfied in a planar 6-gon net or in a three-dimensional structure built from planar zigzag chains, that is, (10,3)-*b* or (10,3)-*c* rather than (10,3)-*a* or (10,3)-*d etc.* We should then associate different nets with various types of sub-unit:

Sub-unit:	Planar zigzag (2₁ axis)	Helical arrays		
	(planar 6-gon net)	3₁	4₁	6₁
Probable three-dimen-sional nets	(10,3)-*b*	(8,3)-*a*	(10,3)-*a*	(12,3)
	(10,3)-*c*	(8,3)-*b*	(10,3)-*d* .	

For example, if threefold helices are the preferred sub-units the (8,3) nets with $Z=6$ are to be expected rather than the (10,3) nets with $Z=4,8$, *etc.* It then follows that for a particular net certain sub-groups may be expected to be less likely than others. In the scheme for less symmetrical versions of the cubic (10,3)-*a* net (where we use Schönflies symbols for brevity) we should not expect to follow the D_3–C_3 route if we associate the net with fourfold helices since this would imply the breakdown of four equivalent points into $(3+1)$ points. Accordingly the space group of H_2O_2 is D_4^4:
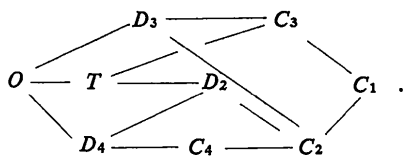
In contrast to the formation of three coplanar bonds in the 4*f* and 5*f* disilicides, silicon forms three pyramidal bonds in combination with the most electropositive elements, the structural chemistry of Si⁻ being very similar to that of the isoelectronic neutral P:

Discrete tetrahedral groups: white P: $(Si_4)^{4-}$ in $BaSi_2$
Planar 6-gon net: black P: $CaSi_2$
Three-dimensional net: –   : $SrSi_2$.

It is not obvious why $SrSi_2$ adopts a structure based on a three-dimensional net rather than, say, a two-dimensional net as in $CaSi_2$, though it is satisfactory that the net selected is one of the two (topologically) simplest three-dimensional 3-connected nets.

The object of this paper and in particular of these concluding remarks is to indicate some of the problems raised by the structures of comparatively simple compounds. If we agree that the structures of solids form an integral part of structural chemistry then this type of crystallochemical enquiry is the logical sequel to studies of the structures of finite molecules in terms of the electronic structures of the component atoms.

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