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SURVEY OF OCTAHEDRAL STRUCTURES AX_n AND A_2X_n

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[Plates 1–4]

CONTENTS

Structures built from octahedral AX_6 groups that share some or all of their X atoms may be classified according to the numbers of octahedra to which the X atoms belong. If v_x is the number of X atoms of each AX_6 group in a structure of composition A_mX_n which are common to x such groups (that is, x is the coordination number of X) then $\Sigma v_x = 6$ and $\Sigma(v_x/x) = n/m$. The solutions of these equations for any composition A_mX_n may be examined systematically. The present survey is restricted to structures in which $m = 1$ or 2 which can be constructed from regular octahedral AX_6 groups all of which share their X atoms in the same way and have no X–X separations shorter than the edge of an octahedron. A study is made of the types of possible structure, finite, one-, two-, or three-dimensional, and the emphasis is on the topology rather than the geometry of the structures.

Introduction

When a new structure is discovered, it is usually possible to compare it only with other *known* structures of a similar type, because a comprehensive survey of the geometrically possible structures has not been made. However, an understanding of the structural chemistry of a particular group of compounds implies that we should understand why certain structures are adopted in preference to others, which can be visualized, but are not adopted by actual compounds. For example, the cubic close-packed octahedral 3D structure which is the idealized structure of the mineral atacamite, $Cu(OH)_3Cl$, is not known for a compound AX_2. Edge-sharing octahedral structures of composition AX_3 based on 3D 3-connected nets are geometrically possible but not observed; neither is one very simple vertex-sharing AX_4 structure to which we refer later. The adoption of more complex chain structures by HfI_4 and ZrI_4 in preference to the simpler chain structures of α-NbI_4 and $TcCl_4$ also emphasizes the need for systematic studies which make possible a comparison of *known* with *unknown* structures having certain specified characteristics.

There is an indefinitely large number of ways of joining together octahedra to form structures which may be finite or extend indefinitely in one, two, or three dimensions. It would be necessary to consider all the possible types of compounds with the formula A_mX_n and then to see how these can arise by sharing vertices, or edges, or faces, or all three. Because of the magnitude of the problem it is necessary to break it down into subdivisions amenable to some kind of systematic treatment. We shall introduce the following restrictions: (i) all octahedra in a structure are topologically equivalent, that is, the arrangement of shared vertices, edges, or faces of each octahedron is the same (or its mirror image if the arrangement is chiral); (ii) it must be possible to build the structure from *regular* octahedra; (iii) all distances between X atoms of different octahedra must be at least equal to the length of the edge of an octahedron. This is what is meant later by 'acceptable X–X distance'. Some consequences of (iii) were explored earlier (Wells 1973).

Each X atom of each AX_6 coordination group is bonded to some number x of A atoms; this number, the coordination number of X, may be different for different X atoms. If v_x is the number of X atoms of each AX_6 group which belong to x such groups, then $\Sigma v_x = 6$ and $\Sigma(v_x/x) = n/m$ in a compound A_mX_n. This survey is restricted to structures in which $m = 1$ or 2. Solutions involving values of x greater than six are omitted from table 1 because no more than six *regular* octahedra can meet at a point while maintaining acceptable X–X distances. (In Th_3P_4, eight distorted octahedral PTh_6 groups meet at each Th atom.) Solutions involving values of v_5 are relevant only for AX_2 ($v_1 = 1$, $v_5 = 5$) and A_2X_3 ($v_2 = 1$, $v_5 = 5$). Structures have been found only for the solutions designated by Roman numerals in the second column of the table.

Our primary classification in terms of the coordination numbers of the X atoms does not provide a convenient means of deriving the arrangements of octahedra that correspond to the solutions of table 1. These structures arise by the sharing of vertices, edges, or faces or all three between the octahedra, and the gross topology of a structure is determined by the number of octahedra to which each is joined. For example, if each octahedron is joined to one other octahedron, by sharing one vertex, edge, or face, the result can only be a finite group of two octahedra. If each octahedron is joined to two others the result is a ring or chain of linked octahedra, and if each is joined to three or more others all four main types of structure are possible, namely, polyhedral groups or structures extending indefinitely in one, two or three dimensions. The present study is therefore a logical sequel to the study of two- and three-dimensional nets.

The connection between octahedral structures and nets is most obvious for the class I structures of table 1, in which each X atom is either unshared (v_1 vertex) or shared between two octahedra (v_2 vertex). The sharing of an X atom between two octahedra may be realized by the sharing of V vertices, E edges, or F faces, it being noted that the values of V and E do *not* include the vertices and edges implied by face-sharing, or the vertices of shared edges. The sum of V, E and F is the number of octahedra to which each is joined, and therefore determines the type of net on which the structure must be based. This approach is illustrated in tables 2, 4, 5, and 6 for structures of composition A_2X_9, AX_4, A_2X_7, and AX_3 respectively.

Reference will be made to a number of 3D three-connected nets. As in the case of two-dimensional nets (tessellations) three-dimensional nets may be described in terms of the smallest polygonal circuits of which they are composed, a circuit being defined as the shortest path starting from a point along one link and returning to the starting-point along another link. In a three-connected net there are three ways of selecting two of the three links that meet at any point and therefore three circuits to be specified for any point. We confine our attention to nets in which the types and arrangement of circuits are the same for all points. That is, there

TABLE 1. OCTAHEDRAL STRUCTURES CLASSIFIED ACCORDING TO THE NUMBERS (v_x) OF x-CONNECTED X ATOMS OF EACH AX_6 GROUP

formula	class	v_1	v_2	v_3	v_4	v_5	v_6
A_2X_{11}	I	5	1	—	—	—	—
AX_5	I	4	2	—	—	—	—
A_2X_9	I	3	3	—	—	—	—
		4	—	—	2	—	—
		4	—	1	—	—	1
AX_4	I	2	4	—	—	—	—
	II	3	—	3	—	—	—
		3	1	—	2	—	—
		3	1	1	—	—	1
A_2X_7	I	1	5	—	—	—	—
	II	2	1	3	—	—	—
	III	2	2	—	2	—	—
		2	2	1	—	—	1
		3	—	—	—	—	3
AX_3	I	—	6	—	—	—	—
	II	2	—	—	4	—	—
	III	1	2	3	—	—	—
	IV	1	3	—	2	—	—
		2	—	2	—	—	2
		2	1	—	—	—	3
		1	3	1	—	—	1
		2	—	1	2	—	1
A_2X_5	I	1	1	—	4	—	—
	II	1	—	3	2	—	—
	III	—	3	3	—	—	—
	IV	—	4	—	2	—	—
		—	4	1	—	—	1
		1	—	4	—	—	1
		1	1	1	2	—	1
		1	1	2	—	—	2
		1	2	—	—	—	3
AX_2	I	—	—	6	—	—	—
	II	—	2	—	4	—	—
	III	1	—	—	—	5	—
	IV	—	1	3	2	—	—
	V	—	2	1	2	—	1
		—	3	—	—	—	3
		—	2	2	—	—	2
		—	1	4	—	—	1
		1	—	—	2	—	3
		1	—	1	—	—	4
A_2X_3	I	—	—	—	6	—	—
	II	—	—	3	—	—	3
	III	—	1	—	—	5	—
	IV	—	1	—	2	—	3
		—	1	1	—	—	4
		—	—	1	4	—	1
		—	—	2	2	—	2
AX		—	—	—	—	—	6

is a configuration of the net that may be described by a set of equivalent points in one of the 230 space groups. If all the shortest circuits are n-gons, the net symbol is n^3. In two dimensions there is the unique 6^3 net, but in three dimensions the series continues with nets 7^3, 8^3, 9^3, 10^3, and 12^3. Moreover, in all cases except 12^3 there are several nets with the same numerical symbol, and it is necessary to distinguish these as n^3-a, n^3-b, and so on. The simplest 3D three-connected nets (those with the smallest possible number (4) of points in the repeat unit) are two different three-dimensional arrays of 10-gons which are designated 10^3-a and 10^3-b; the third net of this family is 10^3-c. This nomenclature for 3D nets is simply an extension of the Schläffli symbols for polyhedra and 2D nets in which, for example, 3^3, 4^3, and 5^3 represent the tetrahedron, hexahedron, and pentagonal dodecahedron, and 6^3 the planar hexagon net. Corresponding to the Archimedean solid (4.6^2) (truncated octahedron), and the 2D net (4.8^2), there are 3D nets: 4.12^2; 4.14^2; and 4.16^2. Here also different nets with the same numerical symbol are distinguished as, for example, 4.14^2-a; 4.14^2-b; and 4.14^2-c. An introduction to nets is available (Wells 1984) and also more detailed treatments (Wells 1977, 1979). Detailed descriptions of structures that are adequately described elsewhere will not be given.

Octahedral structures A_2X_{11}

The only solution ($v_1 = 5$, $v_2 = 1$) corresponds to a pair of octahedra sharing one vertex.

Octahedral structures AX_5

The only solution ($v_1 = 4$, $v_2 = 2$) may be realized in two ways:

(*a*) one vertex may be shared with each of two different octahedra, the shared vertices being either *trans* (a_1) or *cis* (a_2);

(*b*) one edge is shared.

Subgroup a. The possible structures are shown in figure 1. Large rings $(AX_5)_n$, $n \geqslant 12$, could be formed from the *trans* chain a_1, but smaller ones would have unacceptable X–X distances within the rings. In the cyclic systems formed from the *cis* chain a_2, X–X contacts on the outside

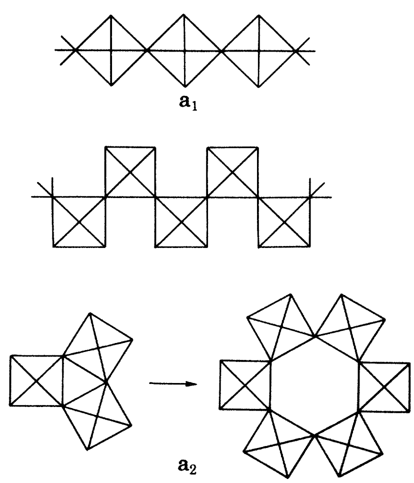
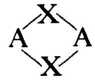


FIGURE 1. Linear and cyclic AX_5 structures.

of the ring set an upper limit ($n = 6$) to the ring size. The cyclic $(AX_5)_4$ represents the molecular structure of a number of pentafluorides.

Subgroup b. A pair of edge-sharing *regular* octahedra has only one configuration, with the four atoms 

coplanar. Since pairs of edge-sharing octahedra appear in various orientations in later figures, four views are shown in figure 2.

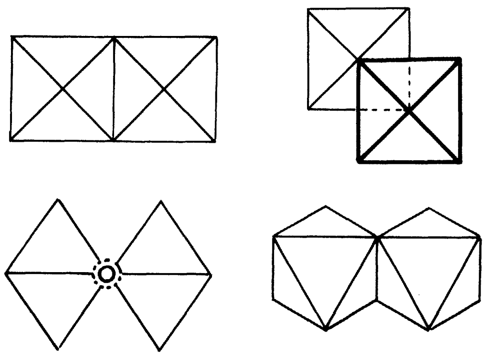


FIGURE 2. Four views of a pair of edge-sharing octahedra.

OCTAHEDRAL STRUCTURES A_2X_9

Of the three solutions listed in table 1 only the first appears to be realizable with regular octahedra, if all share vertices, edges, or faces in the same way. The solution ($v_1 = 4$, $v_4 = 2$) may be eliminated on the following grounds. There are five ways of arranging four *regular* octahedra which meet at a common vertex (figure 3*a–e*), assuming acceptable distances between X atoms of different octahedra, and some or all of the octahedra share *more than* one edge. One vertex of each shared edge is the v_4 vertex; the other must be at least two-connected. The sharing of two or more edges (meeting at the v_4 vertex) implies three or *fewer* v_1 vertices, thus eliminating the solution ($v_1 = 4$, $v_4 = 2$). Note that this restriction applies only to regular

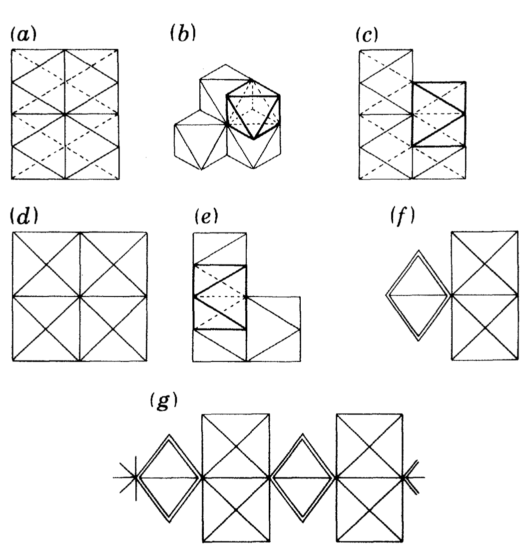


FIGURE 3. Groups of four regular octahedra with a common vertex.

octahedra. In the arrangement (*f*) of figure 3 there are distances between X atoms of different octahedra only 0.76 of the octahedron edge length, and moreover, the above argument does not apply because only one shared edge of each octahedron comes to the v_4 vertex. In fact, this arrangement is found in the 3D anion framework of BaU_2O_7, in which there is appreciable distortion of the UO_6 octahedra (U–O, 1.84 Å (two), 2.12 Å (two), 2.33 Å (two))†. It would give rise to the A_2X_9 chain of figure 3*g*, in which alternate pairs of edge-sharing octahedra are rotated through 90°.

The solution ($v_1 = 4$, $v_3 = 1$, $v_6 = 1$) is not possible for the following reason. There are two possible arrangements of six regular octahedra with a common vertex with acceptable X–X distances. In each of these arrangements, four of the edges of each octahedron that meet at the v_6 vertex are shared edges. Therefore, at least four other vertices of each octahedron must be at least two-connected, or, in other words, there cannot be more than one v_1 vertex in each octahedron.

Structures of class I: $v_1 = 3$, $v_2 = 3$

This solution may be realized in three essentially different ways. An octahedron is joined to three, two, or one octahedra respectively by sharing three separate vertices, one vertex and one edge, or one face. Moreover, in the first two cases there are two arrangements (*mer* and *fac*) of the three shared X atoms (figure 4). There are five types of structure to consider (table 2).

Class I (a).

Subgroup a_1. In this subgroup we find structures of all major types, finite, one-, two-, and three-dimensional. The double chain (ladder) is illustrated in figure 5*a*. The ends of a portion cut from this chain may be joined to form a double ring, but because of X–X contacts within

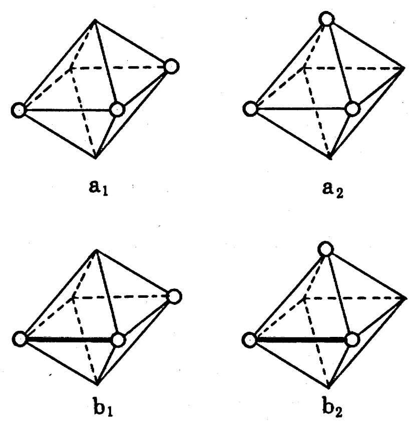


FIGURE 4. Relative positions of shared X atoms (circles) in the subgroups a_1 and a_2 (three vertices shared), and in b_1 and b_2 (one edge and one vertex shared).

TABLE 2. A_2X_9 STRUCTURES OF CLASS I

	V	*E*	*F*
a_1 (*mer*), a_2 (*fac*)	3	—	—
b_1 (*mer*), b_2 (*fac*)	1	1	—
c	—	—	1

† 1 Å = 10^{-10} m = 0.1 nm.

such a double ring each of the two rings must contain at least 12 octahedra, i.e. the formula is $(A_2X_9)_n$ where $n \geqslant 12$. Figure 5*b* shows a portion of a layer based on the 4.8^2 net, and 3D structures include those based on the nets 10^3-b and 10^3-c; the former is illustrated in figure 6.

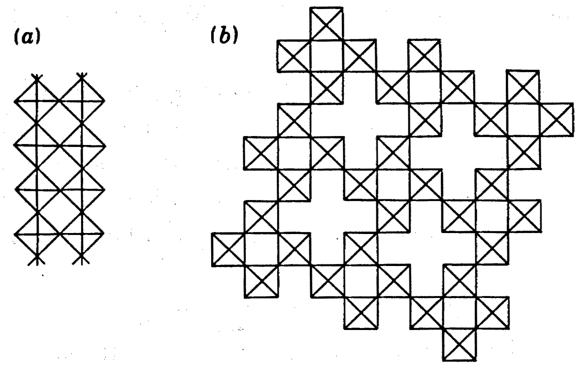


FIGURE 5. A_2X_9 structures of subgroup a_1: (*a*) double chain (ladder); (*b*) layer based on the 4.8^2 net.

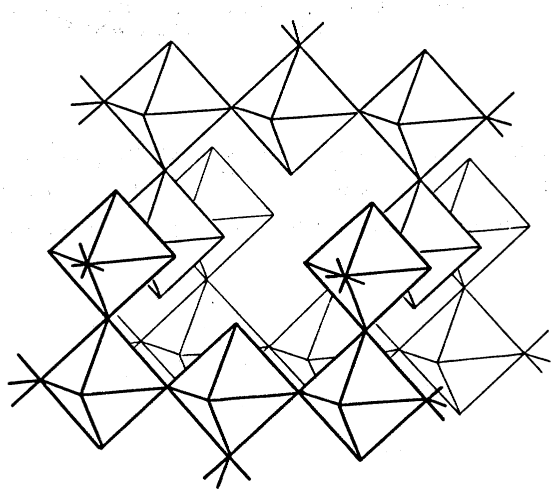


FIGURE 6. A_2X_9 structure based on the net 10^3-b.

Subgroup a_2. These also include three-connected finite, one-, two-, and three-dimensional structures. The three polyhedral complexes based on the three regular three-connected solids (tetrahedron (3^3), cube (4^3), and pentagonal dodecahedron (5^3)), are illustrated in figure 7 and figure 8, plate 1. The second of these A_8X_{36}, is the second member of a family of structures $(A_2X_9)_n$ based on the (three-connected) prisms. In this family the value of *n* is restricted to the values 3, 4, 5, and 6 because in the larger prismatic structures the distance between X atoms of different octahedra becomes less than the edge length. Infinite one-dimensional structures include the double chain (folded ladder) of figure 9, and tubular chains formed from strips of 6^3 and other three-connected nets wrapped around the surface of a cylinder. Layers are based on 2D three-connected nets, and the simplest, based on 6^3 (figure 10), represents the continuation of the family of polyhedral structures based on 3^3, 4^3, and 5^3 noted above. This is the form of the anion in $Cs_3Bi_2Cl_9$. Framework structures can be built based on 3D three-connected nets. In the structures based on the nets 4.14^2-a and 6.10^2 rings of four or

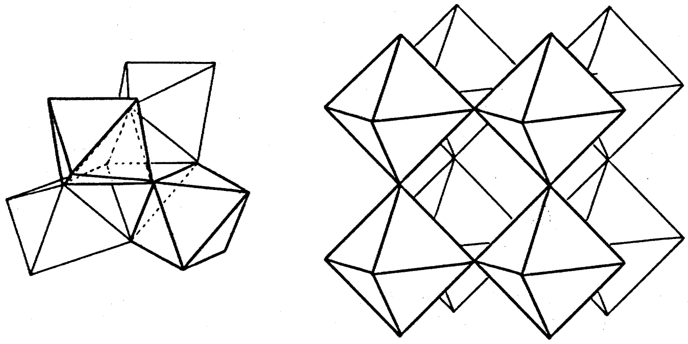


FIGURE 7. The A_4X_{18} and A_8X_{36} complexes of subgroup a_2.

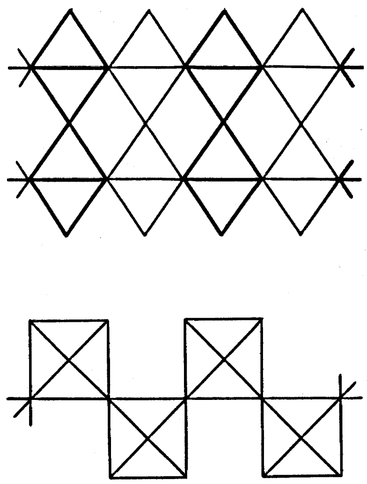


FIGURE 9. Plan and elevation of the double chain $(A_2X_9)_n$ of subgroup a_2.

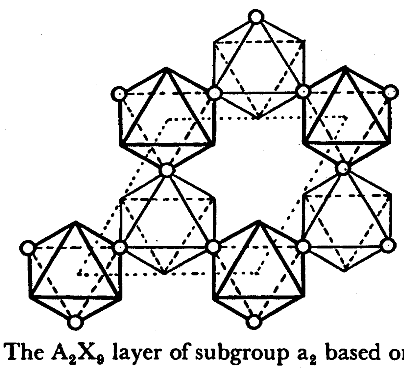


FIGURE 10. The A_2X_9 layer of subgroup a_2 based on the 6^3 net.

six octahedra (figure 11) are joined to form tetragonal or rhombohedral frameworks, a ring replacing a single point in the diamond net or P lattice.

Class I (b)

Subgroups b_1 *and* b_2. Here each octahedron is joined to only two others, and therefore the structures are limited to cyclic or chain structures. Since a pair of edge-sharing octahedra form a rigid group we have to consider the four arrangements of figure 12. All give rise to chains,

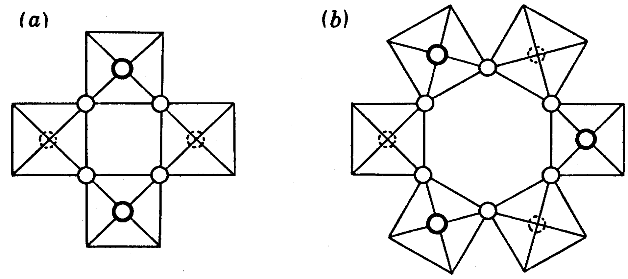


FIGURE 11. Rings of (*a*) four and (*b*) six octahedra in the 3D A_2X_9 structures of subgroup a_2 based on the nets 4.14^2-a and 6.10^2. Circles represent shared X atoms.

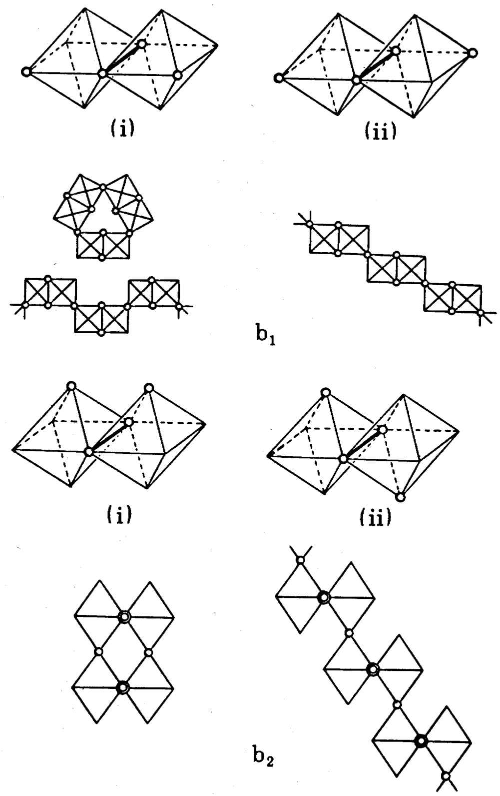


FIGURE 12. The subgroups b_1 and b_2 of A_2X_9 structures. Circles represent shared X atoms.

and b_1(i) also to cyclic structures $(A_2X_9)_n$, $n = 3, 4, 5$, or 6; the upper limit to n is set by contacts between X atoms external to the ring.

Class I (c)

The only structure is the finite A_2X_9 group consisting of a pair of octahedra sharing one face, which represents the structure of molecules and ions such as $Fe_2(CO)_9$, $(Cr_2Cl_9)^{3-}$, and others.

OCTAHEDRAL STRUCTURES AX_4

These include structures of all four major types, finite, and infinite one-, two-, and three-dimensional, and of these only the edge-sharing structures have previously been considered in any detail (Müller 1981). Three solutions of table 1 are closely related to those for tetrahedral AX_2 structures (Wells 1983*a*): but whereas tetrahedral structures of all the three classes of table 3 can be built, it seems that octahedral structures of only the first two classes are possible, though this point is difficult to prove. Assuming this to be true we have only two classes to examine, and we therefore first study how these solutions are realizable as systems of octahedra sharing various combinations of vertices, edges, or faces, alone or in combination.

TABLE 3. TETRAHEDRAL AX_2 AND OCTAHEDRAL AX_4 STRUCTURES

tetrahedral AX_2 structures	v_1	v_2	v_3	v_4	octahedral AX_4 structures	v_1	v_2	v_3	v_4
class I	—	4	—	—	class I	2	4	—	—
class II	1	—	3	—	class II	3	—	3	—
class III	1	1	—	2	—	3	1	—	2

Structures of class I: $v_1 = 2$, $v_2 = 4$

The two-coordination of each X atom can be realized by the sharing of:

(*a*) four vertices, each with a different AX_6 group. The *un*shared vertices may be *trans* (a_1) or *cis* (a_2), when the shared vertices are equatorial (coplanar) or skew (non-coplanar),

(*b*) two edges which have no common vertex; a common vertex would imply a three-connected X atom. Here also there are two subgroups, the shared edges being either *trans* (b_1) or *skew* (b_2),

(*c*) one edge with one octahedron and one vertex with each of two other octahedra. Here two subgroups correspond to those in (*b*), namely, the shared vertices lie at the ends of *trans* (c_1) or *skew* (c_2) edges, but there is also a third possibility (c_3), that the shared edges are in *trans* positions in each octahedron,

(*d*) one face with one octahedron and a fourth X atom with a second octahedron.

These subgroups ae summarized in table 4.

TABLE 4. SUBGROUPS OF CLASS I AX_4 STRUCTURES

subgroup	*V*	*E*	*F*
a_1a_2	4	—	—
b_1b_2	—	2	—
$c_1c_2c_3$	2	1	—
d	1	—	1

Class I (a)

Subgroup a_1. The linking of octahedra through the four coplanar (equatorial) X atoms leads to structures based on 2D and 3D four-connected nets. The simplest layer structure is therefore that based on the square (4^4) net; it represents the layer in SnF_4, NbF_4, and $SnF_2(CH_3)_2$. The simplest 3D structure (figure 13, plate 1) is based on the net 6^48^2, in the most symmetrical (cubic) configuration of which each point is connected to a square coplanar group of nearest neighbours. (If alternate points represent Nb and O atoms, this net represents the structure of NbO.) No example of this AX_4 structure is known. The unit cell may be derived from eight unit cells of the AX_3 (ReO_3) structure, in which AX_6 octahedra share all six vertices, by removing one-quarter of the A atoms. In the most symmetrical configuration of this structure the X atoms therefore occupy three-quarters of the positions of cubic closest packing, as do the O atoms in the ReO_3 structure.

Subgroup a_2. This subgroup includes structures that extend indefinitely in one, two, or three dimensions; some may be derived from A_2X_9 or AX_3 structures by sharing an additional one or two vertices. Thus, reflection if the A_2X_9 ladder or layer of figure 5 across a mirror plane parallel to that of the paper produces a tubular chain or double layer of composition AX_4. One reflection of the *cis* AX_5 chain of figure 1 (a_2) gives the A_2X_9 double chain (folded ladder) of figure 9, while continued repetition gives a corrugated AX_4 layer based on the 4^4 plane net. A square in figure 1 then represents an infinite chain of vertex-sharing octahedra perpendicular to the plane of the paper. The tubular chains $(AX_4)_n$ related in this way to the rings of figure 1 (a_2) are subject to the same limitation as the rings, that is, $n = 3, 4, 5$, or 6 only. The infinite $(AX_4)_{3n}$ chain is the form of the anion in $CsCrF_4$.

The simplest 3D structure formed from octahedra sharing four skew vertices is based on the simplest 3D four-connected net; the diamond net (6^6); it represents the structure of IrF_4 (figure 14, plate 1), in which the underlying diamond net is considerably distorted from its most symmetrical (cubic) configuration. There is a close analogy here with AX_3 structures, which suggests a reason for the adoption by IrF_4 of the much less symmetrical structure in preference to the structure of figure 13. No fluorides adopt the ReO_3 structure, with collinear –X– bonds; instead, they have more compact structures in which the F interbond angle is either close to 150° (as in CoF_3) or 132° (IrF_3). In the latter crystal the F atoms are arranged in one of the most compact ways possible. Instead of occupying three-quarters of the positions of cubic closest packing they are arranged in hexagonal closest packing. For the vertex-sharing AX_4 halide structures there is a similar choice, between the structure of figure 13 with collinear F bonds and the more compact IrF_4 structure, with F bond angle of 132° and hexagonal closest packing of the F atoms. It is interesting to note that in all the halides IrF_3, IrF_4, and IrF_5 the F atoms are arranged in hexagonal closest packing.

Class I (b)

In this class each octahedron is connected to two others, and therefore the only possible structures are rings or chains. From maintaining the usual minimal distance between X atoms of different octahedra, a pair of edge-sharing octahedra is a rigid group. We may accordingly derive the possible structures in class I (b) and I (c) from sub-units consisting of pairs of edge-sharing octahedra.

Subgroup b_1. The sharing of *trans* edges by each octahedron gives the single structure of figure 15 (b_1), the strictly linear NbI_4 chain.

Subgroup b_2. The sharing of *skew* edges (non-opposite, with no common vertex) produces an indefinitely large numer of cyclic and linear structures, the simplest of which were described some years ago (Wells 1970). Relative to a given edge there are four edges which have no vertex in common with the first edge. On an isolated octahedron these four edges are symmetrically equivalent, but the configuration of chain or ring is determined by the choice of pairs of edges of successive octahedra. If we arbitrarily choose one edge of the left-hand octahedron in figure 15 (b_2) as the second shared edge then there are four ways of choosing the second shared edge of the adjacent octahedron. The simplest structures arise if the same relationship is maintained between all successive pairs of octahedra; they are illustrated in figure 16. The pairs of octahedra (i) and (ii) of figure 15 are related by a mirror plane and a centre of symmetry

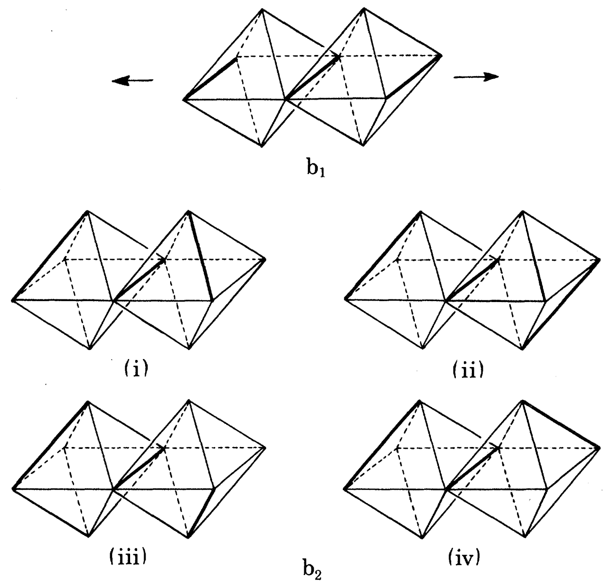


FIGURE 15. Octahedra sharing two edges in the two subgroups of class I(b).

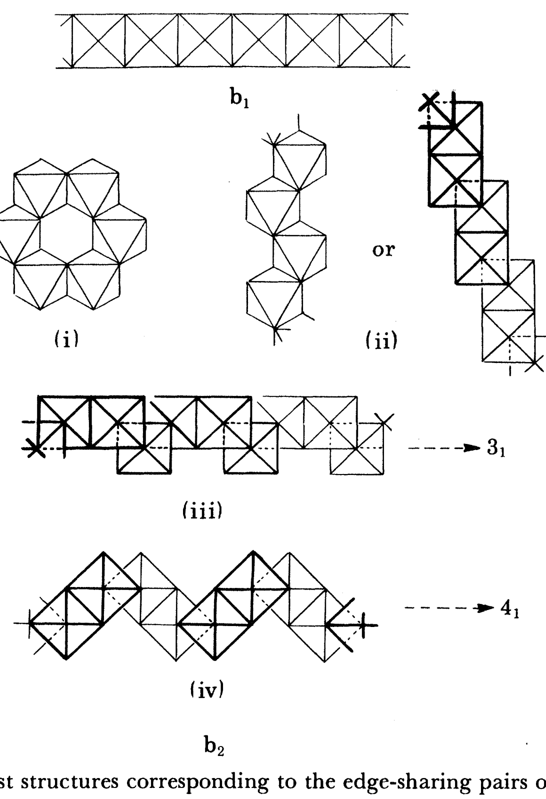


FIGURE 16. The five simplest structures corresponding to the edge-sharing pairs of octahedra of figure 15.

respectively, but (iii) and (iv) are chiral. The chains (iii) and (iv) of figure 16 are accordingly helical, with 3_1 and 4_1 axes respectively. An indefinitely large number of more complex rings and chains are formed from combinations of the sequences (i)–(iv) of figure 15 (b_2), for example, six from sequences such as (i) (ii) ... and 12 from sequences such as (i) (i) (ii) .... A systematic study has been made of those groups of rings and chains (Müller 1981) that are of interest in connection with the structures of halides MX_4. Examples of the structure of figure 16 (b_2) include:

(i) $TeMo_6O_{24}^{6-}$;
(ii) $TcCl_4$, $Li(CuCl_3 . H_2O) . H_2O$;
(iii) —
(iv) $[Na(H_2O)_4]_n^{n+}$ in $Na_2[SiO_2(OH)_2] . 8H_2O$;

and more complex sequences are found in crystalline HfI_4 and ZrI_4.

Class I (c)

This class presents a far greater range of types of structure than class I (b). Since each octahedron is connected to its neighbours by sharing one edge and two vertices, a three-connected system is formed in contrast to the two-connected systems of class I (b). The sub-units include five which correspond to those of I (b): namely, c_1 (one) and c_2 (four), and, in addition, a sixth arrangement of shared vertices c_3 which is not possible in class I (b). These six sub-units are shown in figure 17.

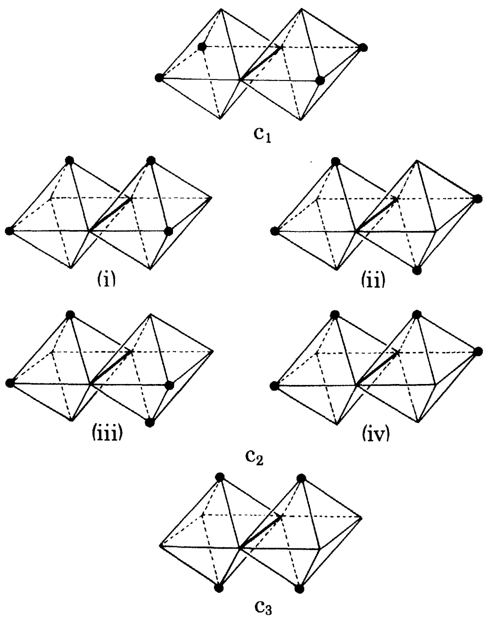


FIGURE 17. Octahedra sharing one edge and two vertices in the three subgroups of class I (c). Shared vertices are shown as small black circles.

Subgroup c_1. The structures in this subgroup are based on three-connected nets, and are obviously of the same topological types as AX_2 structures formed from tetrahedra sharing one edge and two vertices (class I (b) of Wells (1983*a*)). However, some of the structures that can be built from tetrahedra cannot be constructed from octahedra for purely geometrical reasons; these include structures based on three-connected regular or semi-regular polyhedra and the simple three-connected ladder. Figure 18 shows three layers based on the 6^3 plane net, including the two with all six-rings equivalent and one with six-rings of two kinds, and the layers based on the semi-regular nets 4.8^2 and 3.12^2. Structures based on uniform or Archimedean 3D

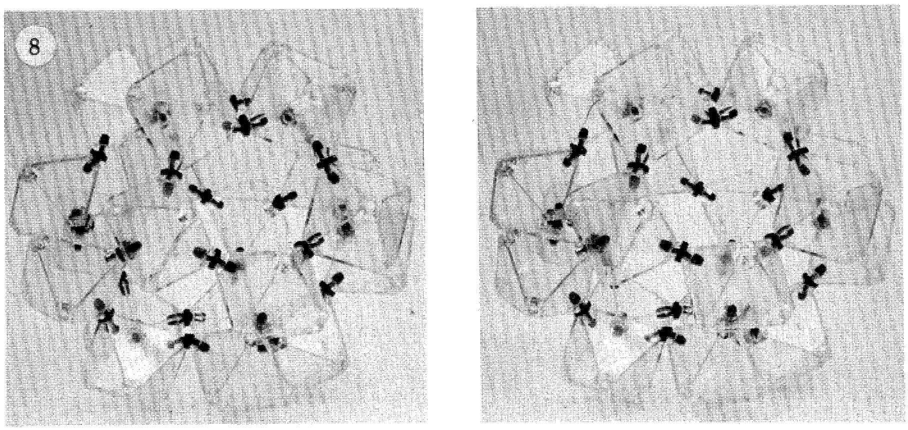


FIGURE 8. The $A_{20}X_{90}$ complex of subgroup a_2. In all stereophotographs of models except figure 14 only *shared* X atoms are shown (as balls or connectors).

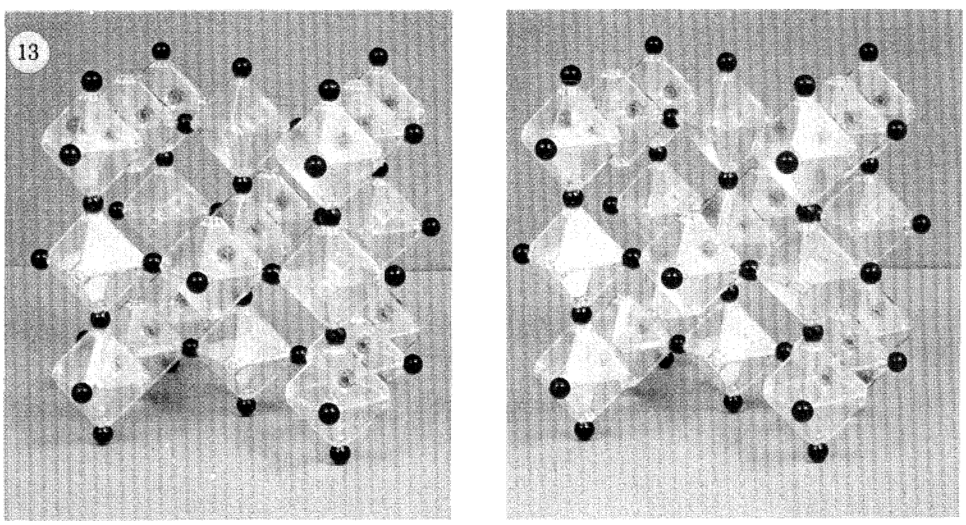


FIGURE 13. Vertex-sharing AX_4 structure of class I (a_1) based on the net 6^48^2.

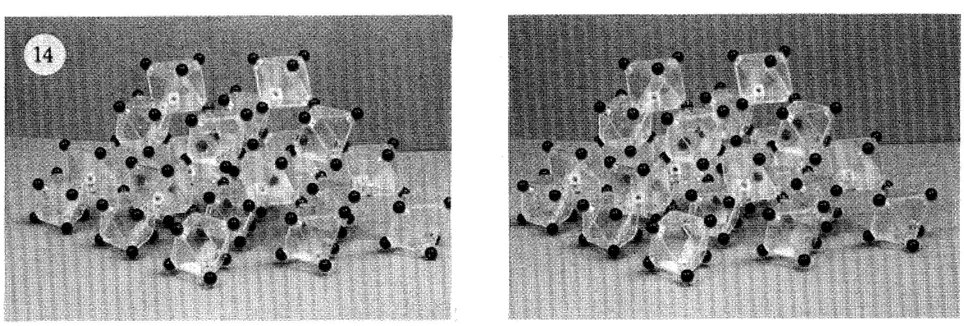
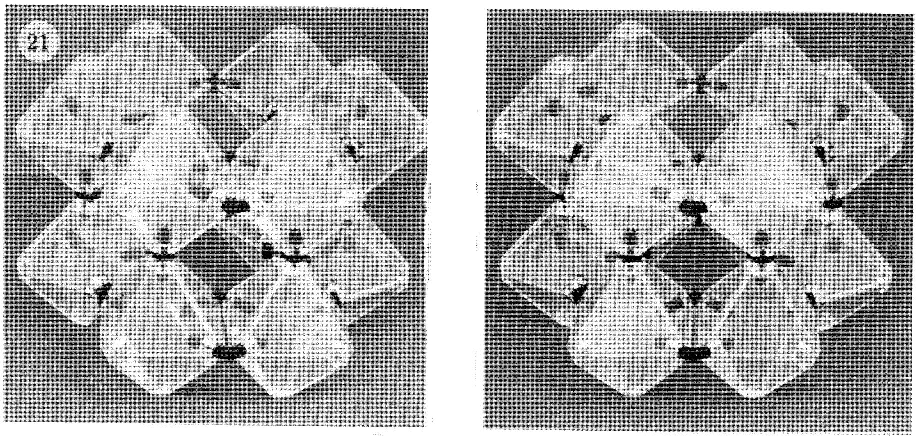
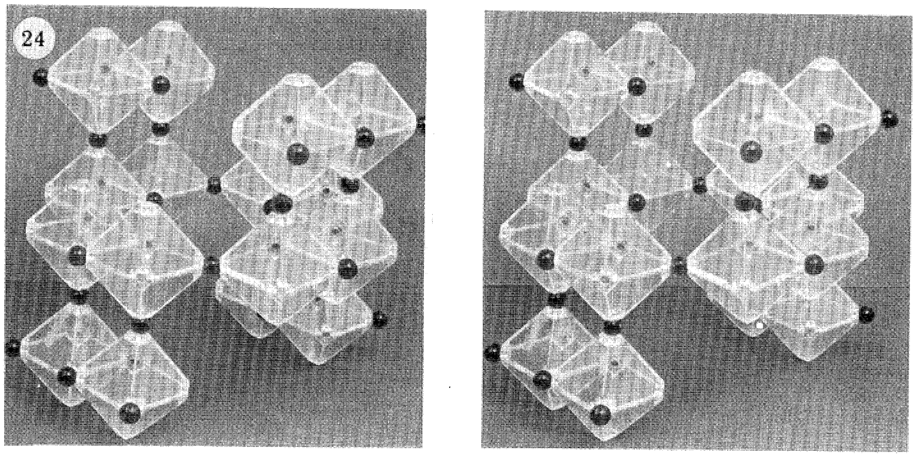
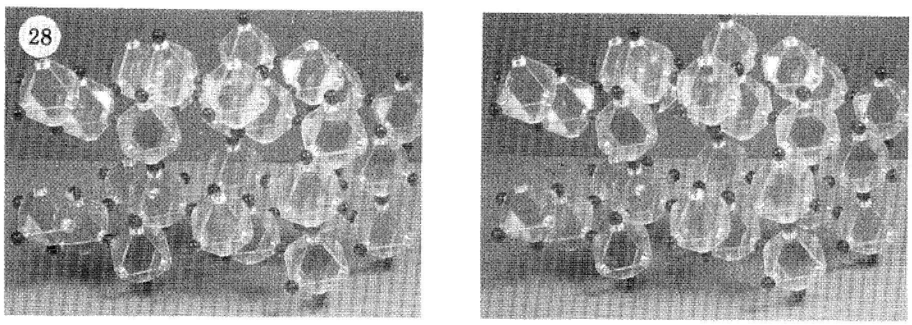
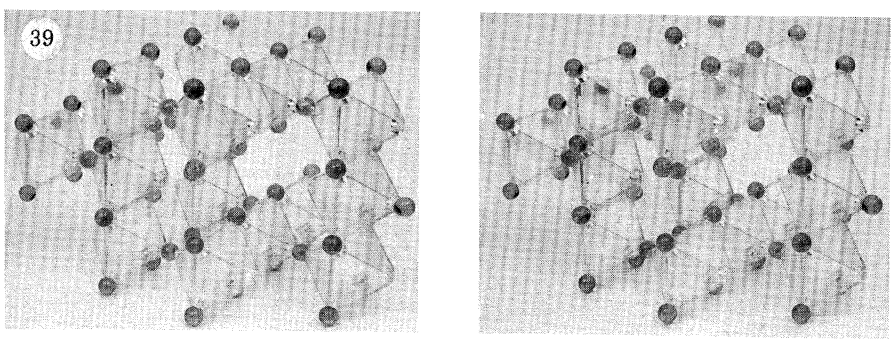


FIGURE 14. The AX_4 structure of class I (a_2) based on the diamond net.









FIGURES 21, 24, 28 and 39. For description see opposite.

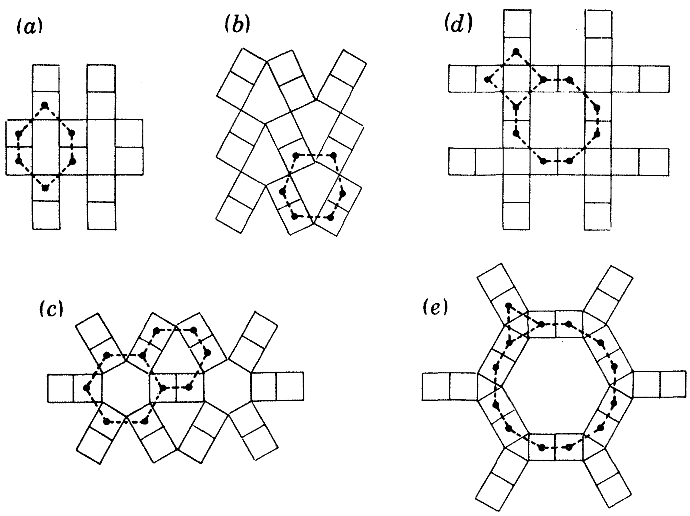


FIGURE 18. Layer structures of class I (c_1) based on three-connected plane nets: (*a*)–(*c*) 6^3, (*d*) 4.8^2, (*e*) 3.12^2. The broken lines connect A atoms and emphasize the underlying three-connected nets.

three-connected nets are also topologically possible, for example, 8^3-b, 9^3-a, and 10^3-b, and one 10-ring of the AX_4 structure based on 10^3-b is shown in figure 19.

Subgroup c_2. This large subgroup gives rise to structures of all four major types, finite, one-, two-, and three-dimensional. We give here examples only of structures built from units all of the same kind, namely, the four c_2 units of figure 17. Units of type (i) joined in pairs give one of the four-octahedral groups of figure 20, with symmetry mm or 2/m. Groups of the type of figure 20*a* may be joined to form a family of prismatic complexes $(A_4X_{16})_n$ in which *n* has the value 3, 4, 5, or 6; the upper limit is set by X–X contacts on the outside surface of the complex. The first member of the family is illustrated in figure 21, plate 2. Alternatively, the four-octahedron unit can form an indefinitely large number of double chains, of which the simplest configuration is that of figure 22. The four-octahedron unit of figure 20*b*, on the other hand, can form 2D and 3D structures. In the layer of figure 23 based on the 4.8^2 net, the edge-sharing pairs of octahedra lie in two parallel planes. An example of a 3D structure is that based on the net 4.8.10-a (Wells 1979, figure 2.4, p. 12). Figure 24 shows the portion of the AX_4 structure which is to be repeated by the translations of a tetragonal body-centred lattice.

The centrosymmetrical units (ii) of figure 17 (c_2) form layers based on the plane nets 6^3, 4.8^2, and 3.12^2, illustrated in figures 25, 26, and 27. Attempts to build a layer based on the third semi-regular plane net, 4.6.12, with acceptable distances between X atoms of different octahedra were not successful. The structure based on the net 10^3-b is shown in figure 28, plate 2.

DESCRIPTION OF PLATE 2

FIGURE 21. Prismatic complex $A_{12}X_{48}$ formed from the sub-unit of figure 20*a*.

FIGURE 24. Sub-unit of the body-centred structure based on 4.8.10-a formed from the four-octahedron group of figure 20*b*.

FIGURE 28. AX_4 structure of class I (c_2)(ii) based on the net 10^3-b.

FIGURE 39. A_2X_7 structure based on the net 10^3-b.

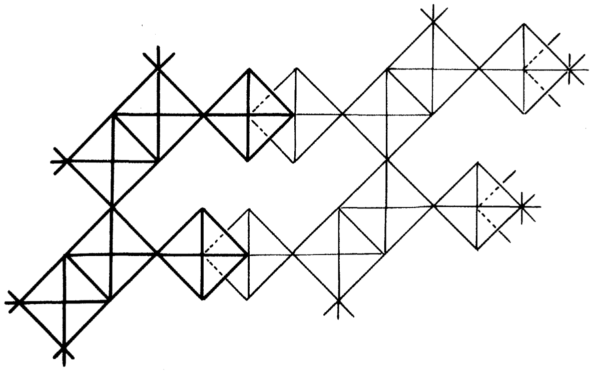


FIGURE 19. One ring of 10 octahedra in the 3D structure based on the net 10^3-b.

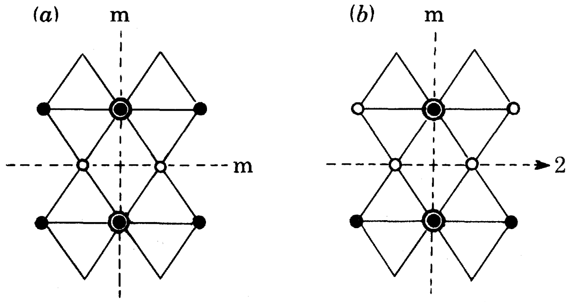


FIGURE 20. Rings of four octahedra of type c_2(i).

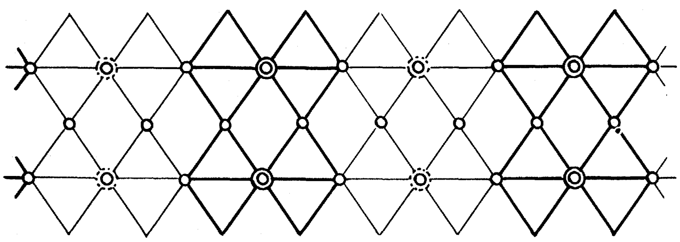


FIGURE 22. Double chain formed from the sub-unit of figure 20*a*.

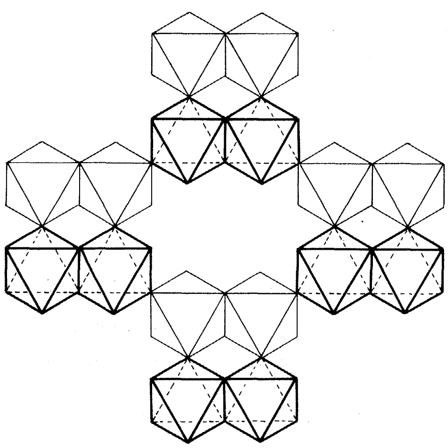


FIGURE 23. Layer of class I (c_2)(i) based on the 4.8^2 net formed from the sub-unit of figure 20*b*.

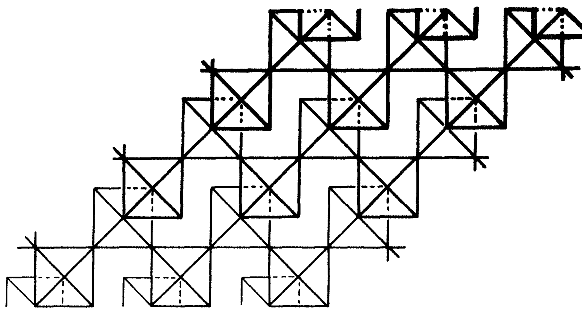


FIGURE 25. Layer of class I (c_2)(ii) based on the net 6^3.

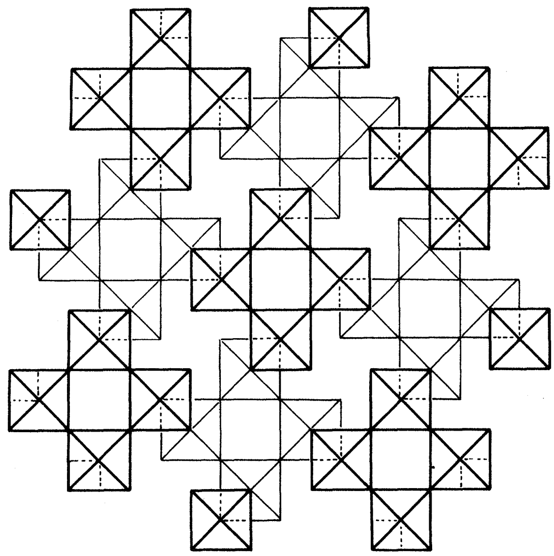


FIGURE 26. Layer of class I (c_2)(ii) based on the net 4.8^2.

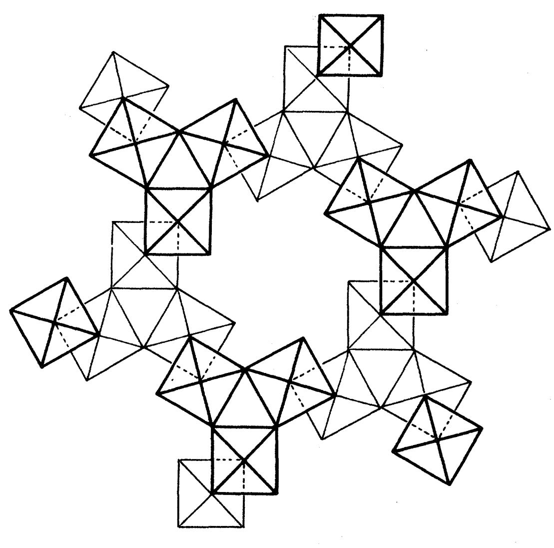


FIGURE 27. Layer of class I (c_2)(ii) based on the net 3.12^2.

An exhaustive study has not yet been made of structures based on the chiral units (iii) and (iv) of figure 17 (c_2); they may include a considerable number of 3D structures. Two 3D structures have been found which are based on the unit (iii). In one the underlying net is a less regular form of 6.10^2, being built of rings of six octahedra of the kind shown in figure 29. A second structure is based on a 4.14^2 net, but this is not the Archimedean net previously

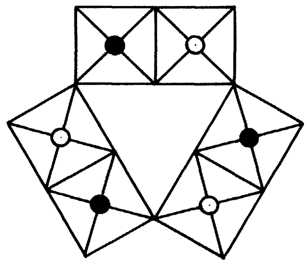


FIGURE 29. Six-membered ring in the structure based on 6.10^2.

described (Wells 1979, p. 10). Two more 4.14^2 nets have now been found (Wells 1983*b*): one tetragonal, the other hexagonal. Like 4.14^2-a the new tetragonal net 4.14^2-b is derived from the diamond net by replacing points by four-rings, but in the most symmetrical configuration of 4.14^2-b successive four-rings lie in perpendicular planes, in contrast with 4.14^2-a in which the planes of all four-rings are parallel. A model of the octahedral structure may be built from chains of the kind shown in figure 30. These are to be superposed in perpendicular directions to produce rings of four octahedra the planes of which are normal to that of the paper. One ring of four (vertex-sharing) octahedra is shown at the centre of figure 31, where the groups of four octahedra at the left and right are at different levels, as indicated by the line thicknesses.

Three different rings of four octahedra may be constructed from the unit (iv) and its enantiomorph (iv)*, namely, the rings made from two (iv) or two (iv)* units, which we

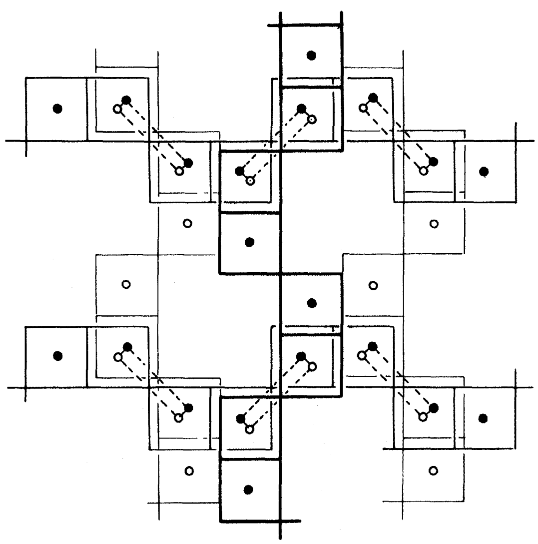


FIGURE 30. Projection of portion of structure based on 4.14^2-b showing chains at three levels. These are slightly displaced relative one to another to show the rings of four octahedra (broken lines) normal to the plane of the paper. The small circles represent shared X atoms in the four-membered rings.

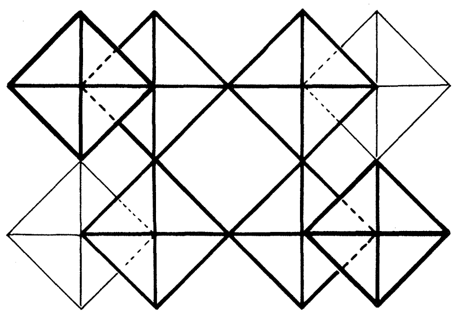


FIGURE 31. Four c_2(iii) sub-units forming the vertex-sharing ring of four octahedra in the structure based on $4 . 14^2$-a.

designate $(iv)_2$ and $(iv)_2^*$, and the ring made from one (iv) and one (iv)*. The last, (iv) (iv)*, has symmetry 2/m. These three rings (figure 32) differ from that of figure 31 in that alternate junctions are shared edges and shared vertices. The rings $(iv)_2$ form a structure based on the net $4 . 14^2$-b, while alternate $(iv)_2$ and $(iv)_2^*$ rings form a structure based on $4 . 14^2$-a. The rings (iv) (iv)* form an indefinitely large number of double chains, of which the simplest is shown in figure 33.

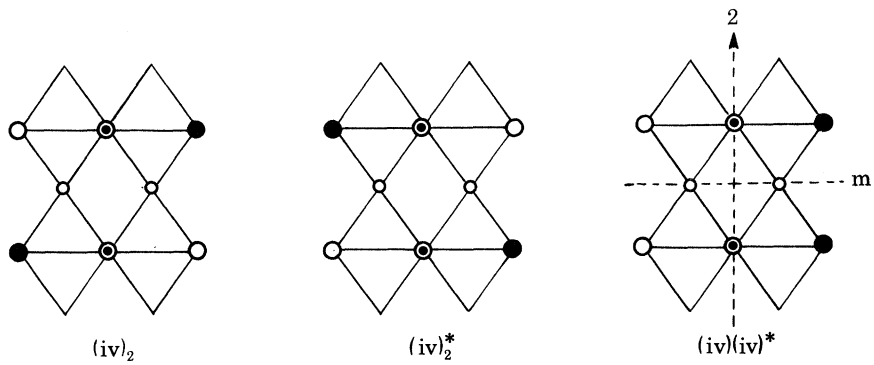


FIGURE 32. The three rings of four octahedra formed from the sub-units c_2(iv) and its enantiomorph (iv)*.

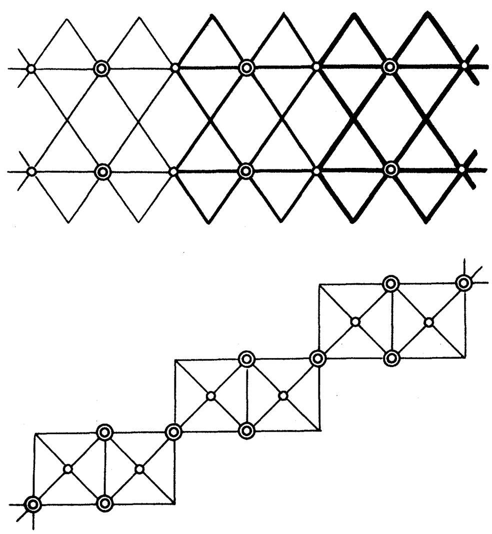


FIGURE 33. Plan and elevation of the double chain formed from sub-units (iv)(iv)*.

Subgroup c_3. The unit c_3 of figure 17 forms the double chain of figure 34, an example of which is the structure $NbOCl_3$. The O atoms are at the shared *trans* vertices of each octahedron. Owing to the relative positions of the shared vertices no other structures are possible.

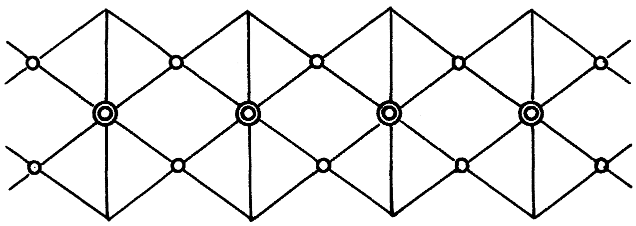


FIGURE 34. The double chain of class I (c_3).

Class I (d)

Since the terminal X atoms of a pair of face-sharing octahedra lie at the vertices of a trigonal prism there are two ways of selecting one terminal X atom of each octahedron (figure 35*a*). Each type of face-sharing pair gives rise to a variety of chain and cyclic structures. The simplest ones formed from the symmetrical sub-unit shown at the left in (*a*) are illustrated at (*b*) and (*c*). The smallest cyclic structure is $(A_2X_8)_3$ and the largest is $(A_2X_8)_6$ if all the A atoms are coplanar, as at (*c*), because of contacts between X atoms of different octahedra.

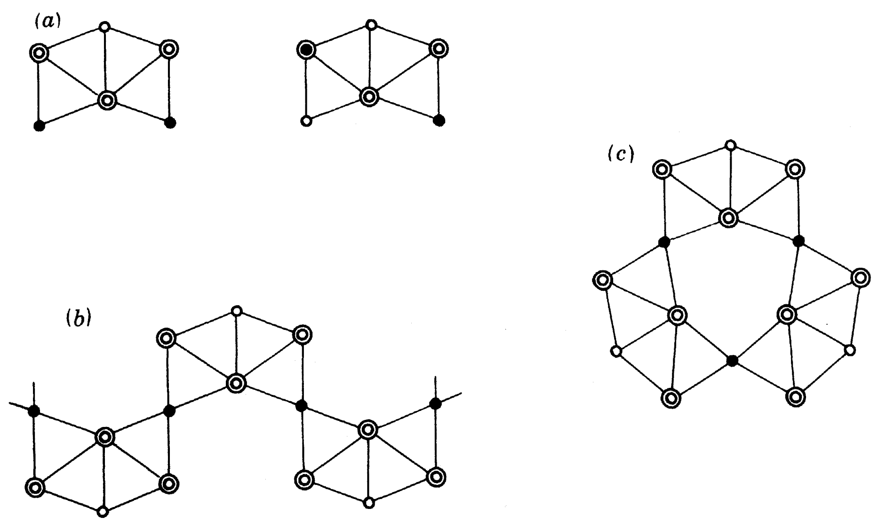


FIGURE 35. Structures of class I (d): (*a*) the two face-sharing pairs of octahedra which have to share the terminal X atoms shown as black circles; (*b*) chain $(AX_4)_n$; (*c*) cyclic complex $(A_2X_8)_3$.

Structures of class II: $v_1 = 3$, $v_3 = 3$

There are two ways of selecting three vertices of an octahedron, and each corresponds to only one structure with acceptable X–X distances. If the three shared vertices belong to one face the tetrahedral A_4X_{16} complex, of which two views are shown in figure 36*a*, is formed. This is the idealized structure of the $TeCl_4$ tetramer. The other possible structure is the double chain of figure 36*b*, of which no example appears to be known.

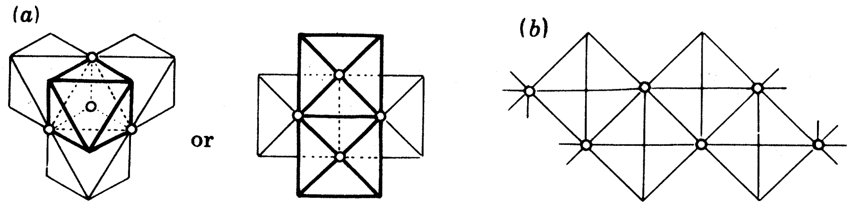


FIGURE 36. (a) Two views of the finite complex A_4X_{16}. (b) The chain $(AX_4)_n$ of class II.

OCTAHEDRAL STRUCTURES A_2X_7

Of the solutions listed in table 1 only three appear to be realizable, and these present a great variety of structures; those in classes I and II are especially numerous.

Structures of class I: $v_1 = 1$, $v_2 = 5$

The sharing of five X atoms of each octahedron between two octahedra may be achieved in the ways shown in table 5.

TABLE 5. SUBGROUPS OF CLASS I A_2X_7 STRUCTURES

		V	*E*	*F*	
class I	a	5	—	—	
	b	3	1	—	
	c_1	1	2	—	(*trans* edges)
	c_2				(*skew* edges)
	d	2	—	1	
	e	—	1	1	

Class I (a)

Double layers consisting of two layers of octahedra can be cut from the ReO_3 structure or from the tetragonal and hexagonal bronze structures, perpendicular to the (001) axis in each case. The simplest layer of this type, from the ReO_3 structure, represents the structure of the anion in $Sr_3Ti_2O_7$. The double layer projects as figure 5*a*, each square then representing a vertex-sharing chain of octahedra perpendicular to the plane of the paper. A 3D framework structure is formed from the A_2X_9 layer of figure 5*b* by sharing the vertices above and below the plane of the A atoms. This is the ReO_3 structure from which one-fifth of the Re atoms together with the intervening O atoms have been removed as linear rows perpendicular to the plane of the layer: $Re_5O_{15} - ReO = Re_4O_{14}$.

Class I (b)

There are two arrangements of the three shared vertices relative to the shared edge, and therefore in an edge-sharing pair of octahedra there are the four arrangements of shared X atoms shown in figure 37. The two octahedra are related either by a mirror plane or by a centre of symmetry.

The arrangement (i) gives double layers formed from, and projecting as, the AX_4 layer of figure 18 in which the two layers are related by a mirror plane. The centrosymmetrical arrangement (ii), on the other hand, forms 3D structures derived from the more complex layers of figures 26 and 27. If pairs of these layers are related by mirror planes parallel to the plane

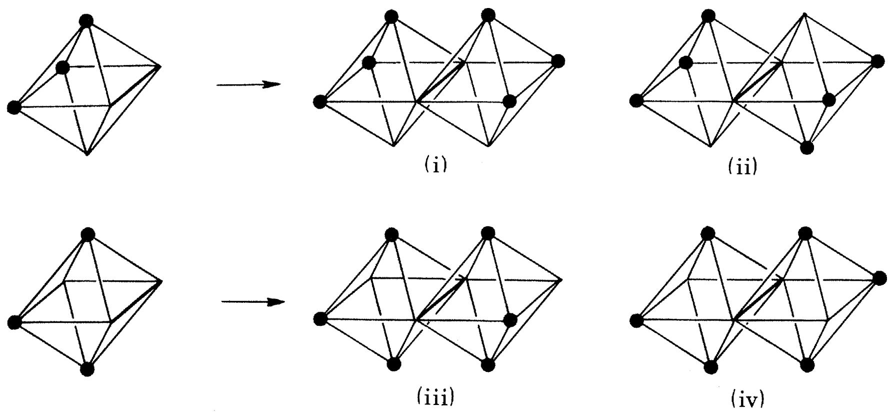


FIGURE 37. The four subgroups of A_2X_7 class I (b).

of the paper, cubical or trigonal prismatic groups of octahedra are produced respectively. These groups are joined by sharing octahedron edges. Each octahedron is then connected to four others, one by edge-sharing and three by vertex-sharing. The underlying nets, the connected systems of A atoms, on which the structures are based are the four-connected nets 4^38^3 and 3.4^28^3 (Wells 1979, figs 3.26 and 3.9 respectively).

The arrangements (iii) and (iv) correspond to (i) and (ii) of b_1 in figure 12, with additional sharing of all four polar X atoms in each case. The structures therefore correspond to those in b_1, these illustrations now being projections of structures extending indefinitely in a direction perpendicular to the plane of the paper. They are accordingly tubular chains and layers built from $NbOCl_3$-like chains. For the tubular chains $(A_2X_7)_n$ n is restricted to the values 3, 4, 5, and 6 as already noted for the cyclic $(A_2X_9)_n$ structures.

Class I (c)

In the subgroup c_1 (sharing of *trans* edges), only two arrangements of the shared vertices in the strictly linear chain are permissible (figure 38); all others bring in contact X atoms that are not to be bonded when the chains are joined by sharing the fifth vertex of each octahedron.

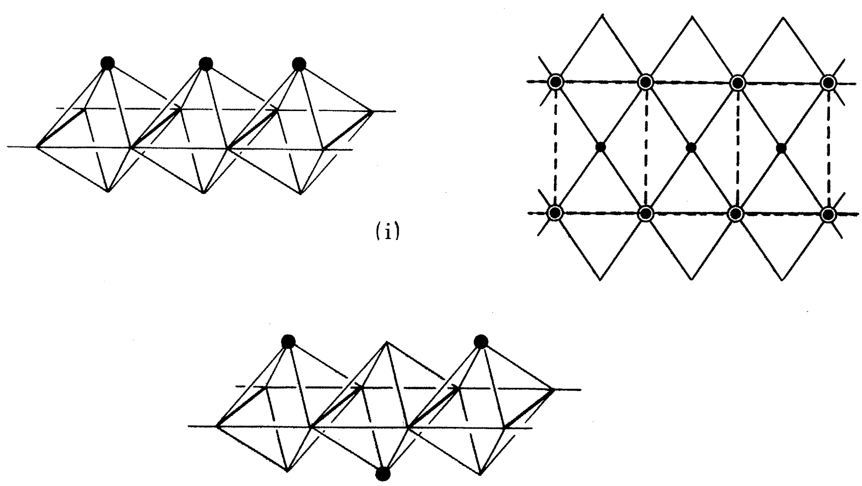


FIGURE 38. The two permissible arrangements of the shared vertices in class I (c_1).

With all shared X atoms on the same side of the chain (figure 38 (i)), the only structure is the double chain shown at the right in which the connected system of A atoms (ladder) is the simplest infinite three-connected system. In structures derived from (ii), with shared X atoms alternately on opposite sides of the chain, the chains must be inclined to one another, as in the 3D structures based on the nets 10^3-b and 10^3-c; structures based on 2D nets are not possible. The structure based on 10^3-b is shown in figure 39, plate 2.

Structures in the subgroup c_2 (sharing of *skew* edges) are derivable from the AX_4 structures of figure 16. The subgroup is of outstanding interest as providing examples of structures based on all the following three-connected nets:

2D: 6^3; 4.6.12;

3D: 8^3-a; 10^3-a; 6.10^2.

The A_6X_{24} ring of figure 16 (i) may be linked by vertex-sharing to produce a configuration of the 2D 4.6.12 net in which equal numbers of six-rings lie in two parallel planes (figure 40) or a 3D structure based on 6.10^2 (figure 41). The *skew* chain of figure 16 (ii) forms structures based on two configurations of the 6^3 net (figure 42). As may be seen from the elevations of these layers all shared vertices are coplanar in both layers. The helical *skew* chains (iii) and (iv) of figure 16 are generated by 3_1 and 4_1 axes respectively, and give structures

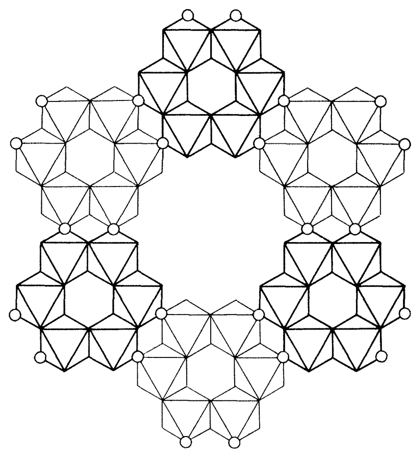


FIGURE 40. A_2X_7 structure of class I (c_2) based on the net 4.6.12.

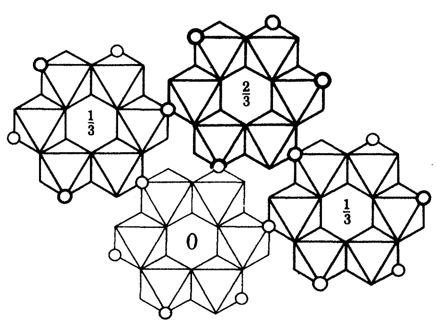


FIGURE 41. A_2X_7 structure of class I (c_2) based on 6.10^2.

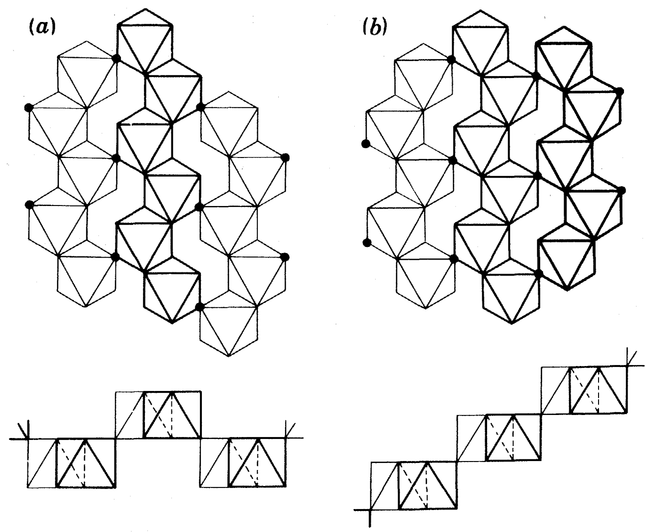


FIGURE 42. Two configurations of the A_2X_7 layer of class I (c_2) based on 6^3. Circles represent shared X atoms.

based on the 3D three-connected nets 8^3-a and 10^3-a. A projection of the 8^3-a structure is shown in figure 43 and a stereo-pair in figure 44, plate 3. Figure 45, plate 3, shows the structure based on 10^3-a.

Class I (d)

For a pair of octahedra that share one face and two vertices there are the two arrangements of the two shared vertices shown in figure 46*a* and *b*; the former is dissymmetric (*a* and *a**). Each octahedron is joined to three others, by a face and two vertices. Of the structures based on 2D nets we show in figure 46*c* the layer formed from *b*. Structures based on 3D three-connected nets are probably numerous, for structures based on, for example, 10^3-b can be built from (*a*), (*a*) + (*a**), and (*b*). The second of these is illustrated as a stereo-pair in figure 47, plate 3. This class of A_2X_7 structures is related to class I (g) of AX_3 structures:

AX_3 class I (g): 1 face, 1 edge, and 1 vertex shared;
A_2X_7 class I (d): 1 face, 2 vertices shared, 1 vertex unshared.

We have therefore labelled figure 46*a* and *b* to correspond to figure 62*a* and *b*.

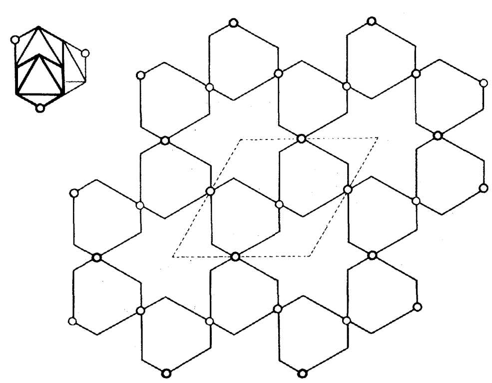


FIGURE 43. Projection of the A_2X_7 structure of class I (c_2) based on 8^3-a. At top left is shown a projection of the 3_1 helical chain (AX_4 *skew* chain) from which the 3D structure may be built.

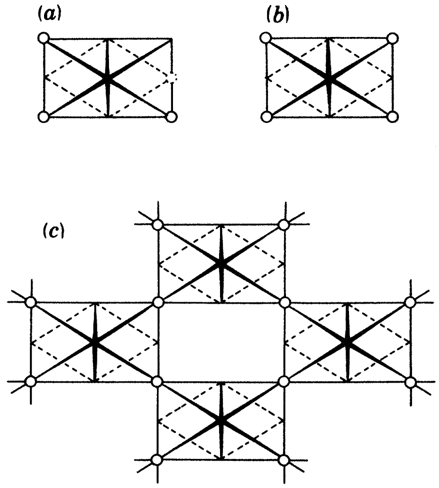


FIGURE 46. (a) and (b). The two arrangements of shared vertices in class I(d) of A_2X_7 structures. (c) A_2X_7 layer of type (b).

Class I(e)

As each octahedron is joined to two others, only rings or chains are possible (figure 48). Only the ring of five pairs of octahedra ($A_{10}X_{35}$) has acceptable X–X distances within and outside the ring. The chain is the form of the cation–water complex in $[Na_2(H_2O)_7]HAsO_4$.

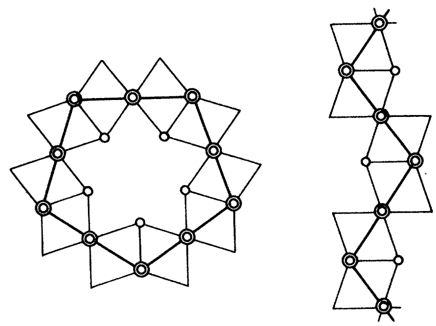


FIGURE 48. The cyclic complex $A_{10}X_{35}$ and the $(A_2X_7)_n$ chain of class I(e).

Structures of class II: $v_1 = 2$, $v_2 = 1$, $v_3 = 3$

The three arrangements of the three types of vertex, which correspond to the isomers of a finite complex Ma_2bc_3, are illustrated in figure 49. The three subgroups are: (*a*) $3v_3$ *mer*, $2v_1$ *trans*; (*b*) $3v_3$ *mer*, $2v_1$ *cis*; (*c*) $3v_3$ *fac*. Structures found in this class include finite, 1D, and 2D structures.

Class II(a)

The only structure found is the planar layer of figure 50. Since each octahedron is joined to three others, by sharing two edges (with a common vertex) and one vertex, the structure is based on a three-connected net, here the simplest such net, 6^3. One six-ring is indicated by the black dots, which represent A atoms.

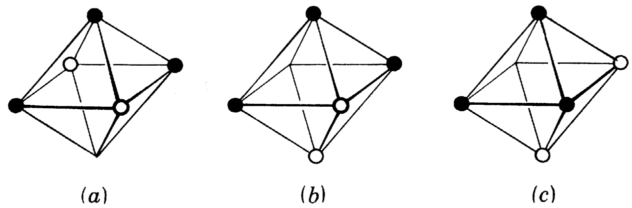


FIGURE 49. Arrangements of the three types of vertex in class II. The open and filled circles represent one- and three-connected vertices respectively.

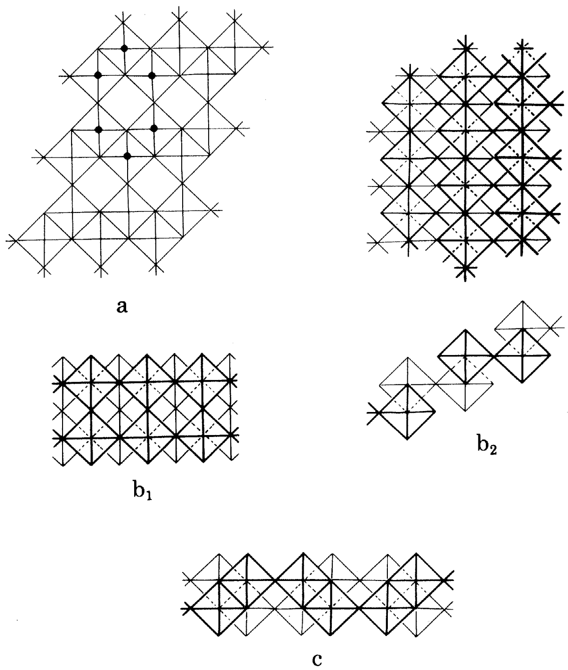


FIGURE 50. A_2X_7 structures of class II (a), (b), and (c).

Class II (b)

The layer of figure 50 (a) is built of AX_4 chains (figure 36*b*) joined laterally to convert one v_1 to a v_2 vertex. The same chains may be joined to form two other structures which are based on the (three-connected) ladder, figure 50 (b_1), and 6^3 net, figure 50 (b_2). In the layer there are rings of four vertex-sharing octahedra, but the topology must take account of the edge-sharing since certain pairs of octahedra are joined only in this way. The layer is therefore properly described as based on the 6^3 net.

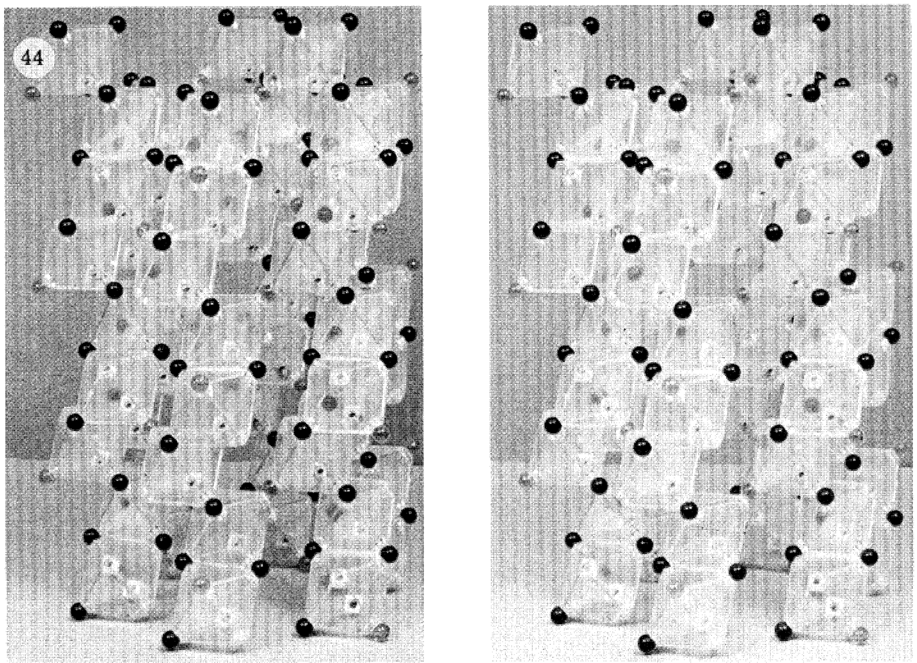
DESCRIPTION OF PLATE 3

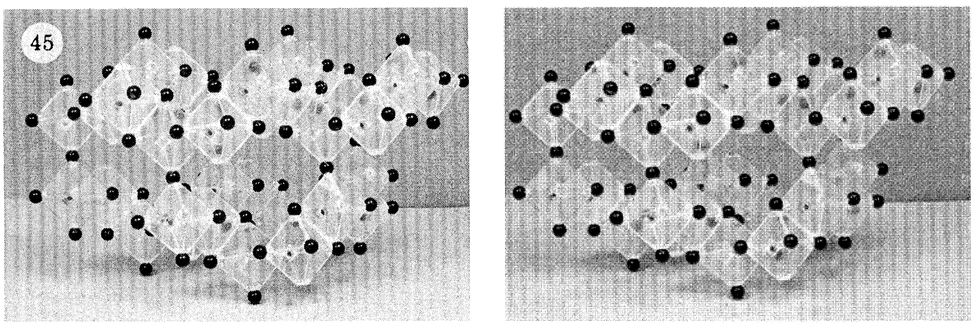
FIGURE 44. Portion of the A_2X_7 structure of figure 43.

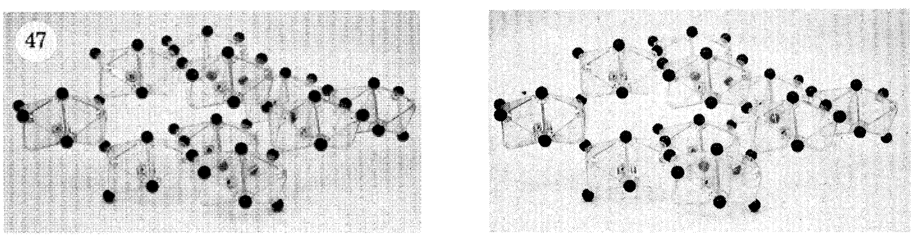
FIGURE 45. A_2X_7 structure of class I (c_2) based on 10^3-a.

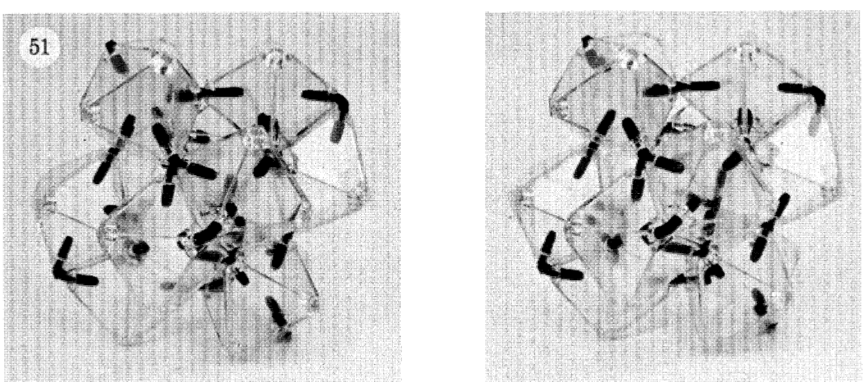
FIGURE 47. A_2X_7 structure of classI (d) based on 10^3-b.

FIGURE 51. The finite $A_{12}X_{42}$ complex of class II (c) based on the icosahedron.









FIGURES 44, 45, 47 and 51. For description see opposite.

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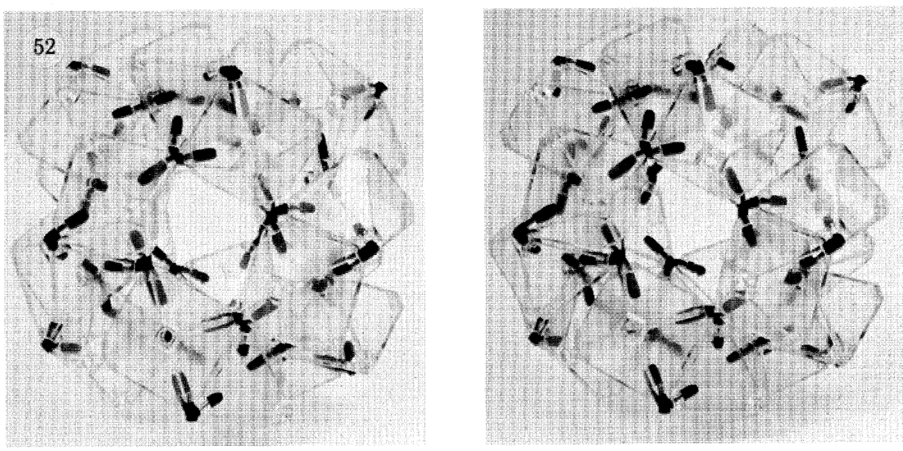
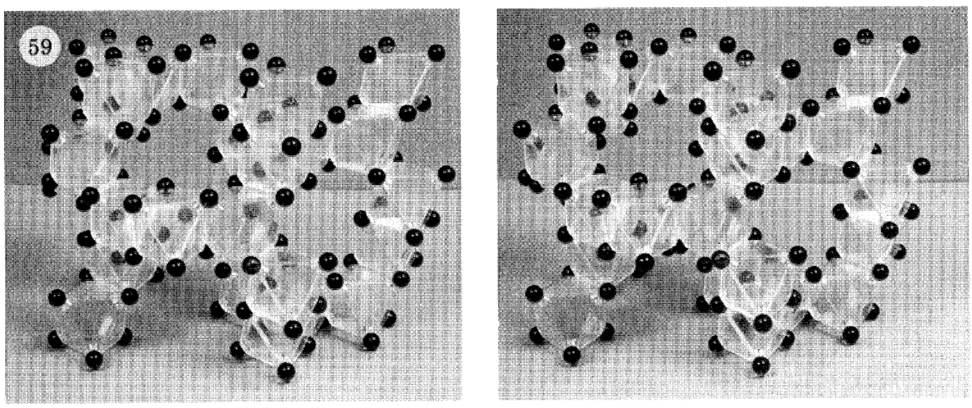
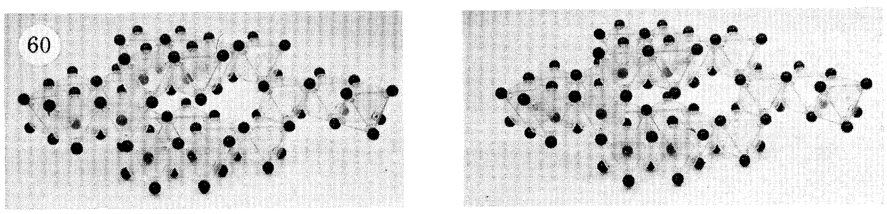
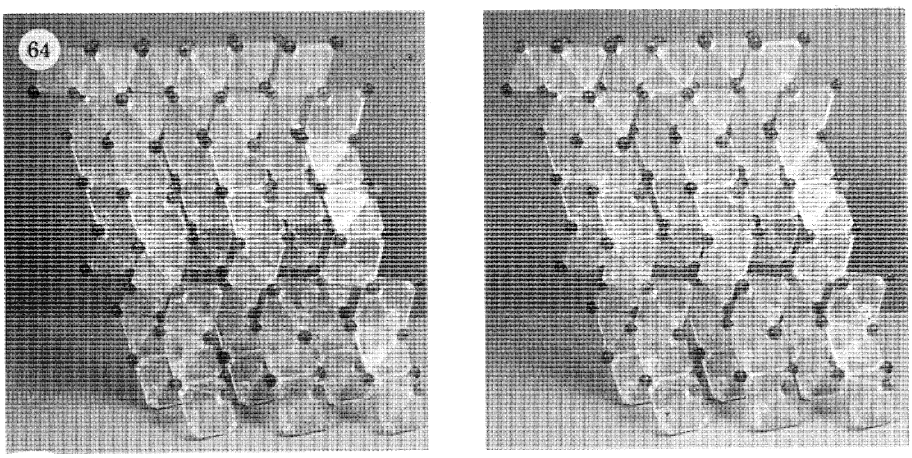








FIGURES 52, 59, 60 and 64. For description see opposite.

Class II (c)

Two entirely different types of structure are possible if the three v_3 vertices belong to one face. One is a structure based on a five-connected polyhedron with pairs of edge-sharing triangular faces meeting at each vertex; the relevant polyhedra are the icosahedron, snub cube, and snub dodecahedron. Pairs of face-sharing octahedra form the polyhedral complexes $A_{12}X_{42}$ (figure 51, plate 3) and $A_{24}X_{84}$ (figure 52, plate 4) based on the icosahedron and snub cube respectively. Only the former has acceptable X–X distances on the outside of the complex when constructed from regular octahedra, but we illustrate the snub cube structure (which has some short X–X distances) since the octahedra in an actual structure would be distorted owing to the face-sharing. The $A_{60}X_{210}$ complex based on the snub dodecahedron cannot be built from regular octahedra. These structures may be compared with those derived from paris of *edge*-sharing *tetrahedra* based on the same polyhedra (Wells 1983 *a*). A structure of a second type in this subgroup is the infinite chain of figure 50c.

Structures of class III: $v_1 = 2$, $v_2 = 2$, $v_4 = 2$

There are five possible arrangements of the three kinds of vertex, and of these only one corresponds to a structure which can be constructed with regular octahedra. This is the double chain of figure 53, which is simply a strip of the AX_3 layer of figure 65. We have already

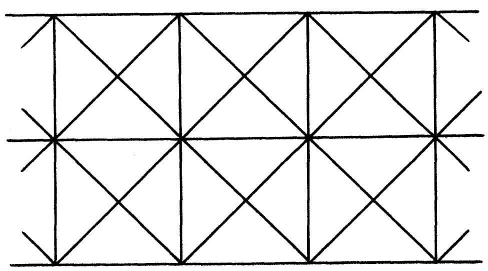


FIGURE 53. A_2X_7 double chain of class III.

mentioned the A_2X_7 framework found as the structure of the anion in BaU_2O_7. This is formed from rutile chains joined at alternate O atoms to similar chains running in perpendicular directions. The junction points (v_4 vertices) are of the kind shown in figure 3*f*, an arrangement not to be expected for regular octahedra.

DESCRIPTION OF PLATE 4

FIGURE 52. The complex $A_{24}X_{84}$ based on the snub cube.

FIGURE 59. AX_3 structure of class I (d) based on 10^3-a.

FIGURE 60. AX_3 structure of class I (d) based on 10^3-b.

FIGURE 64. AX_3 structure of class I (g) based on 10^3-b.

Octahedral structures AX_3

As no structures have been found involving vertices common to six octahedra there are four classes to consider.

Structures of class I: $v_2 = 6$

This is by far the most important class of AX_3 structures, and includes nearly all the known structures built from octahedral coordination groups. The sharing of each X atom between two octahedral AX_6 groups may be realized as in table 6 by sharing various numbers of vertices V, edges E, or faces F; or all three. In (c) and (d) the shared edges must have no vertices in common, and in (g) the shared edge and face must have no vertex in common.

Table 6. Subgroups of class I AX_3 structures

		V	E	F
class I	a	6	—	—
	b	4	1	—
	c	2	2	—
	d	—	3	—
	e	—	—	2
	f	3	—	1
	g	1	1	1

Class I (a)

Structures in which each X atom of each AX_6 group is shared with another (different) group are based on six-connected nets. The simplest is therefore based on the P lattice, and in its most symmetrical form is the cubic ReO_3 structure. In this structure, the X atoms occupy three-quarters of the positions of cubic closest packing, but there are less symmetrical variants with denser packings of the X atoms, the limit being a structure with hexagonal closest packing of these atoms. Structures based on more complex six-connected 3D nets include those of tungsten bronzes and the BX_3 framework in the pyrochlore structure of compounds $A_2(B_2X_6)X$.

Class I (b)

The sharing of one edge gives a pair of octahedra that form a rigid unit, if the usual restriction on distances between X atoms of different octahedra is assumed; this sub-unit has eight unshared vertices. Sharing of the two pairs of *trans* vertices of each octahedron leads to a double chain (as $NbOCl_3$) and these double chains can then be joined by sharing the remaining vertices to form 3D structures. The projections of these structures (figure 54) are similar to the AX_4 layers formed from octahedra sharing one edge and two vertices (figure 18). Each edge-sharing pair in figure 54 represents the projection of an infinite chain perpendicular to the plane of the paper. Figure 54*a* represents the idealized projection of the anion framework of $CaTa_2O_6$.

Alternatively, the remaining vertices of each edge-sharing pair of octahedra may be shared as four pairs (figure 55). The arrangement of these vertices is such that a 3D framework based on the NbO net is formed; this is the anion framework of $KSbO_3$.

Class I (c)

In structures of this subgroup the two shared edges may not have a common vertex, since this would lead to a three-coordinated X atom ($v_3$vertex) and the shared vertices may be *trans* (c_1) or *cis* (c_2). The sharing of *trans* vertices (and therefore of opposite edges) leads only to a

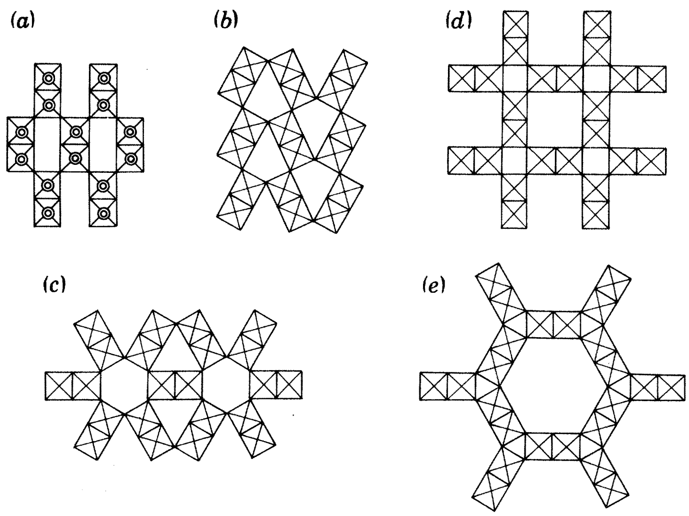


FIGURE 54. Projections of 3D AX_3 structures of class I (b).

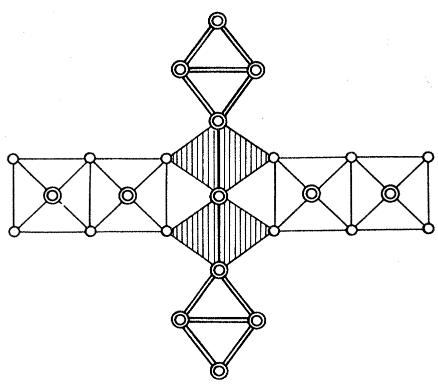


FIGURE 55. Arrangement of four edge-sharing pairs of octahedra around one pair in the 3D anion framework of $KSbO_3$ (class I (b)).

layer based on the simplest four-connected net, 4^4. This layer (figure 56) is found in the closely related minerals duttonite, VO_2OH, and paraduttonite, $VO(OH)_2$. In the subgroup c_2 each octahedron shares two *cis* vertices and two *skew* edges, and the irregular tetrahedral disposition of these vertices and edges leads to a 3D structure based on the diamond (6^6) net. Like the AX_2 structures of anatase and niobite (or α-PbO_2) it can be built of chains of octahedra sharing two *skew* edges (the AX_4 chain of $TcCl_4$), and these chains are emphasized in figure 57, where this AX_3 structure is compared with that of anatase. In the AX_3 structure of figure 57*a* the chains are joined by vertex-sharing, instead of by further edge-sharing as in the AX_2 structures. No example is known of this AX_3 structure, which in a geometrical sense is intermediate between the anatase and IrF_4 structures, all being based on the diamond net (table 7).

Class I (d)

The sharing of three edges (with no common vertices) leads to the well known AX_3 layer of numerous trihalides and trihydroxides which is based on the 6^3 net (figure 58). The mid-points of the shared edges are coplanar with the A atom and therefore structures can be built which

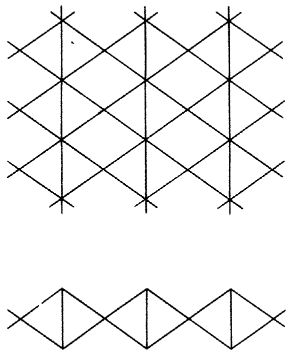


FIGURE 56. Plan and elevation of the AX_3 layer of class I (c_1).

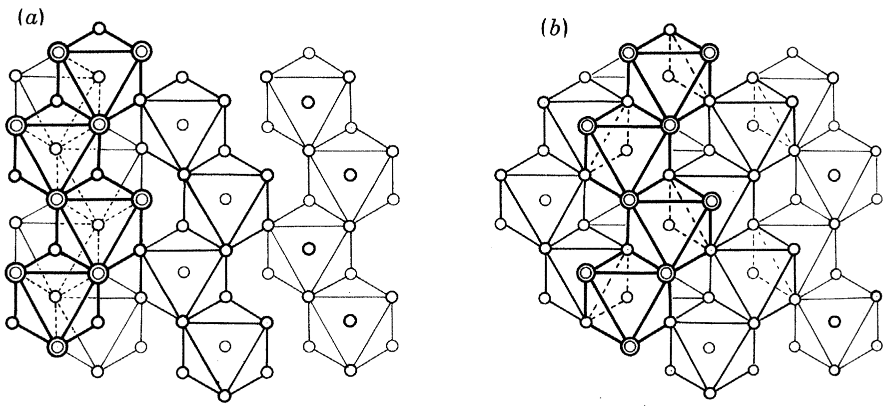


FIGURE 57. (*a*) The 3D structure of class I (c_2) based on the diamond net. (*b*) The structure of anatase (TiO_2).

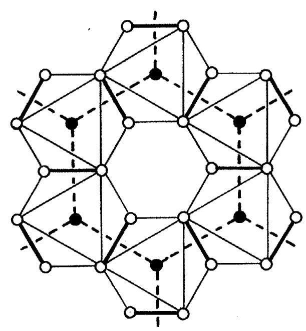


FIGURE 58. The edge-sharing AX_3 layer of class I (d). The heavy full lines represent shared edges, and the broken lines indicate the underlying 6^3 net.

TABLE 7. THREE STRUCTURES BASED ON THE DIAMOND NET

structure	composition	octahedra sharing	packing of X atoms
anatase	AX_2	4 edges	c.c.p.
figure 57*a*	AX_3	2 edges 2 vertices	c.c.p.
IrF_4	AX_4	4 vertices	h.c.p.

are based on the most symmetrical forms of the simplest 3D three-connected nets, 10^3-a, -b, and -c. In the structure based on the cubic net 10^3-a, the X atoms occupy three-quarters of the positions of cubic closest packing, as in the ReO_3 structure, while in the edge-sharing structure based on 10^3-b there is cubic closest packing of the X atoms. No examples are known of compounds with these structures (illustrated in figures 59 and 60, plate 4).

Class I (e)

The sharing of two opposite faces of each octahedral AX_6 group leads only to the infinite chain structure of ZrI_3 and other trihalides.

Class I (f)

The sharing of one face and three vertices of each AX_6 group results in the very simple structure shown in plan and elevation in figure 61. Each hexagon in the projection represents a pair of face-sharing octahedra, the shared faces being at heights 0 and $\frac{1}{2}c$. The X atoms occupy

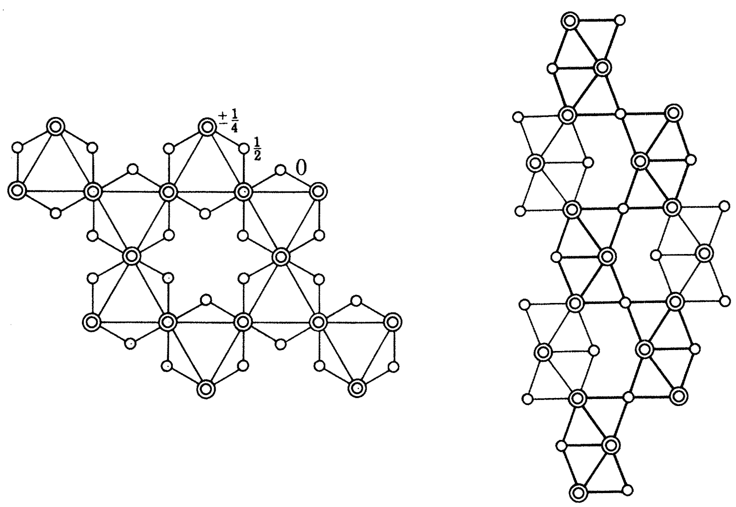


FIGURE 61. Plan and elevation of the 3D structure of class I (f).

three-quarters of the positions of *hc* (ABAC...) packing. No example appears to be known of an AX_3 compound with this structure, but it represents the octahedral anion framework of high-$BaMnO_3$, in which the Ba^{2+} ions complete the closest-packed layers of composition BaO_3.

Class I (g)

The sharing of one vertex, one edge, and one face of each AX_6 octahedron might seem an unnecessarily complicated way of attaining the formula AX_3, but appears less so when compared with the structure of, for example, ThI_4, in which eight-coordination groups share one edge and two faces to form a layer based on the 6^3 net. Structures in this class are based on three-connected nets, for each octahedron is connected to three others. There are two ways (figure 62) of selecting the shared vertex of each octahedron (small black circle) since the shared edge must not have a vertex which is also a vertex of the shared face. No structures based on the arrangement of figure 62*a* have been found, but structures of type (*b*) include layers based on the 2D nets 6^3, 4.8^2, and $4.6.12$ (figure 63), and a 3D structure based on 10^3-b

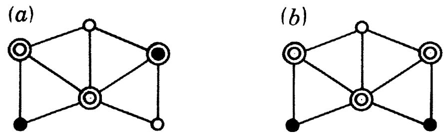


FIGURE 62. The two ways of selecting the shared vertices in class I (g).

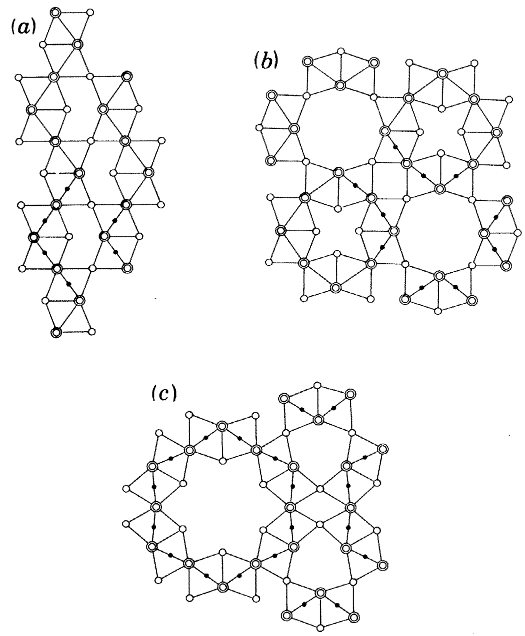


FIGURE 63. Layers in class I (g) based on the plane nets 6^3, 4.8^2, and $4.6.12$.

(figure 64, plate 4). In figure 63 the underlying three-connected nets are emphasized by showing some of the A atoms as black dots.

Structures of class II: $v_1 = 2$, $v_4 = 4$

The two subgroups correspond to *trans* (i) or *cis* (ii) arrangements of the two *un*shared X atoms. The only structures appear to be: (i) the layer formed when each octahedron shares the four equatorial edges (figure 65), as in the anion in $NH_4(HgCl_3)$, and (ii) the multiple chain of figure 66. No example of this chain seems to have been reported.

Structures of class III: $v_1 = 1$, $v_2 = 2$, $v_3 = 3$

Examples of three structures in this class are known. The possible arrangements of the three kinds of vertex correspond to the isomers of an octahedral complex Mab_2c_3 (figure 49). However, in both (*b*) and (*c*) the v_2 vertices are in *cis* positions and therefore can be shared either as separate vertices (with different octahedra) or as an edge (with the same octahedron). There are, accordingly, five cases to consider, and each gives rise to a layer structure (figures 67–71). There is a further complication, namely, that case (*c*) can be realized in a third way (in the double-chain anion of the NH_4CdCl_3 structure (figure 72)). These subgroups are summarized in table 8.

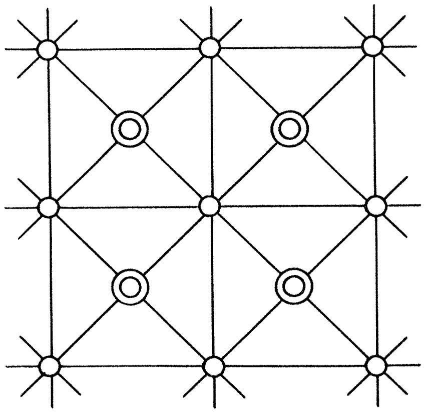


FIGURE 65. The class II (i) layer structure of the anion in NH_4HgCl_3.

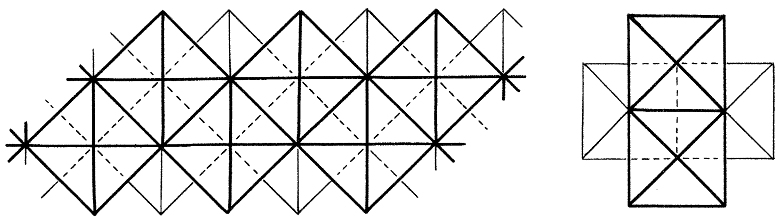
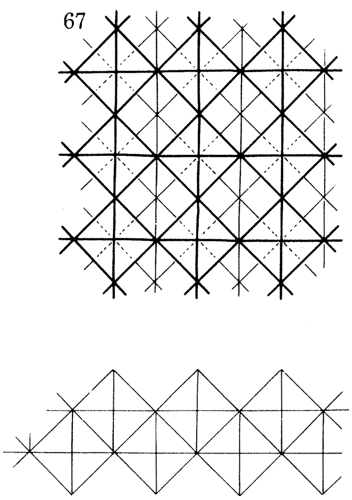


FIGURE 66. The multiple chain of class II (ii) with end-on view at right.

67



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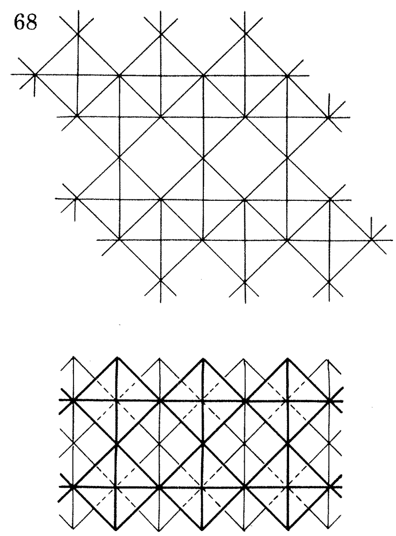

FIGURE 67. The layer of class III (a), plan and elevation.
FIGURE 68. The layer of class III (b_1), plan and elevation.

Structures of class IV: $v_1 = 1$, $v_2 = 3$, $v_4 = 2$

There are three arrangements of the three kinds of vertex, analogous to those of figure 49*a*, *b* and *c*. No structures corresponding to (*a*) (v_4 *trans*) have been found, but those of types (*b*) and (*c*) include a number of structures that may be built from octahedra sharing a pair of *skew* edges (as in the cyclic $TeMo_6O_{24}^{6-}$ ion or the skew chain), or a pair of opposite edges ('rutile

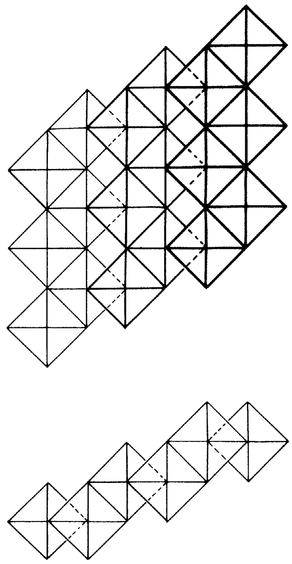

Figure 69. The layer of class III (b_2), plan and elevation.

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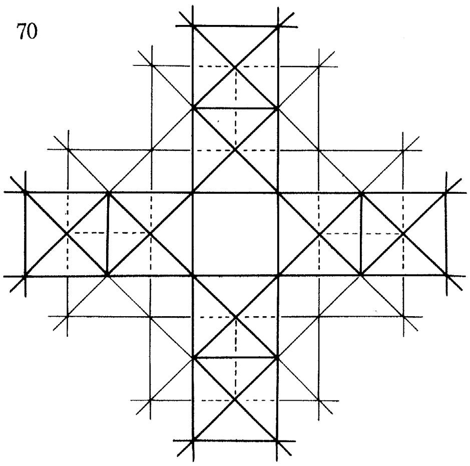

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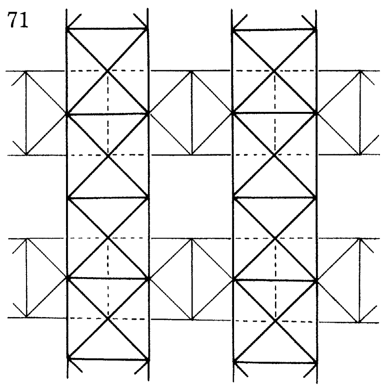


Figure 70. The double layer of class III (c_1).
Figure 71. The double layer of class III (c_2).

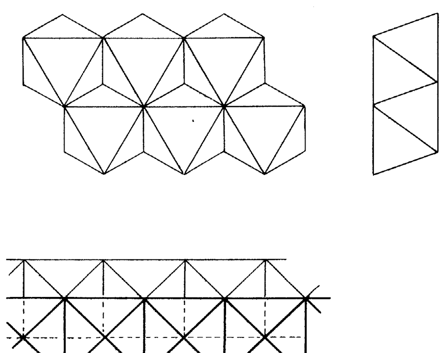


Figure 72. Two views of the double chain of class III (c_3) and end-on view.

chain'). In the subgroup b we have the finite group $A_{12}X_{36}$, formed from two parallel rings of six octahedra (as in $TeMo_6O_{24}^{6-}$) joined by sharing one face of each octahedron, and the double chain formed from two skew chains in a similar way. The analogous double chain formed by joining two rutile chains laterally by face-sharing (figure 73*a*) belongs to the subgroup c. This subgroup also includes the fourfold chain (figure 73*b*) and the corrugated layer of figure 73*c*, these structures being formed when each octahedron of the rutile chain shares a third edge and also one vertex. In the views of the multiple chains shown at the right of figure 73*a* and *b* and also in the layer of figure 73*c* the rutile chains are perpendicular to the plane of the paper.

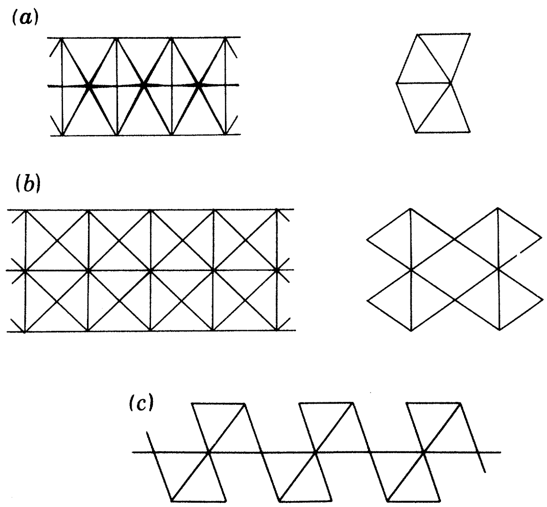


FIGURE 73. AX_3 structures of class IV (see text).

TABLE 8. AX_3 STRUCTURES OF CLASS III

	figure	example
a	67	MoO_3
b_1	68	—
b_2	69	$Th(Ti_2O_6)$
c_1	70	—
c_2	71	—
c_3	72	$NH_4(CdCl_3)$

OCTAHEDRAL STRUCTURES A_2X_5

Of the solutions listed in table 1, four appear to be realizable as structures built from regular octahedra.

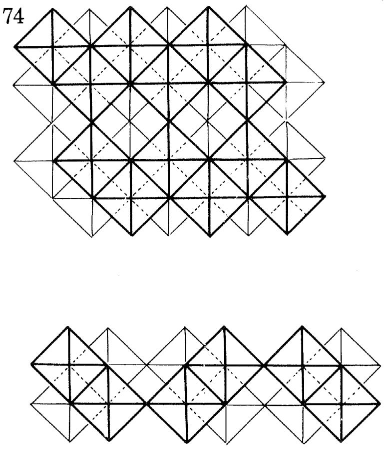
Structures of class I: $v_1 = 1,\ v_2 = 1,\ v_4 = 4$

This class is closely related to class II AX_3 ($v_1 = 2,\ v_4 = 4$), the change involving only the conversion of one of the v_1 vertices into a v_2 vertex. As in class II AX_3 there are two arrangements of the vertices: (i) v_1 and v_2 *trans*, and (ii) v_1 and v_2 *cis*.

Subgroup (i). Two AX_3 layers of figure 65 may share all of their vertices that project to one side of the layer to form a double layer which has the same projection as the single layer.

Subgroup (ii). The AX_3 chain of figure 66 can share one more vertex of each octahedron to form the layer shown in plan and elevation in figure 74 or the very simple 3D structure shown in projection in figure 75. The unit cell of this latter structure contains only $2(A_2X_5)$.

74



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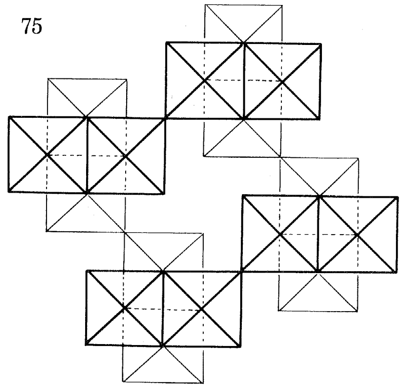


FIGURE 74. Plan and elevation of A_2X_5 layer of class I (ii).
FIGURE 75. Projection of 3D A_2X_5 structure of class I (ii).

Structures of class II: $v_1 = 1$, $v_3 = 3$, $v_4 = 2$

The possible arrangements of the three kinds of vertex are those of figure 49, but structures have been found with only one of the three arrangements, namely, *fac* of figure 49*c*. The structures found are layers formed from double edge-sharing ('rutile') chains, which are perpendicular to the plane of the paper in figure 76.

Structures of class III: $v_2 = 3$, $v_3 = 3$

Structures in this class may be derived from AX_3 structures of class III ($v_1 = 1$, $v_2 = 2$, $v_3 = 3$) by joining the v_1 vertices of pairs of octahedra. The possible arrangements of vertices are only (*a*) *mer* and (*b*) *fac*, but in (*a*) we may distinguish two cases: (a_1) the three v_2 vertices are shared as separate vertices (with three other octahedra), or (a_2) two of the v_2 vertices are shared as an edge. The A_2X_5 structures are related to the AX_3 structures of class III as in table 9. The two layers of figures 67 and 68 may be joined through the v_1 vertices to form the same 3D A_2X_5 structure, projections of which, in two perpendicular directions, are the same as the projections of the layers (upper diagrams in figures 67 and 68). This is the idealized structure of V_2O_5, built of regular octahedra. The 3D A_2X_5 structure formed from the AX_3 layer of figure 69 is shown in figure 77. In the 3D A_2X_5 structures formed from the double AX_3 layers of figures 70 and 71 pairs of double layers are related by mirror planes, and therefore the

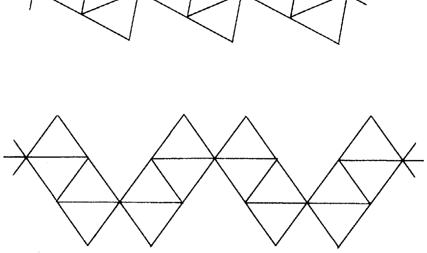
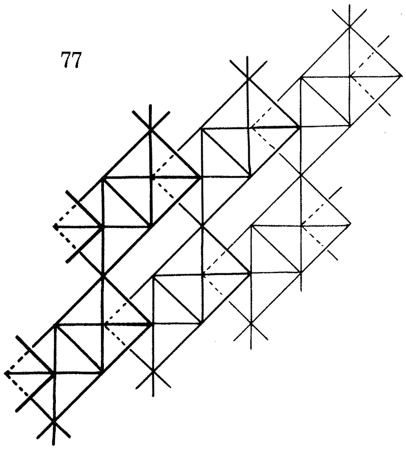


FIGURE 76. Elevation of A_2X_5 layer of class II built from double rutile chains.

77



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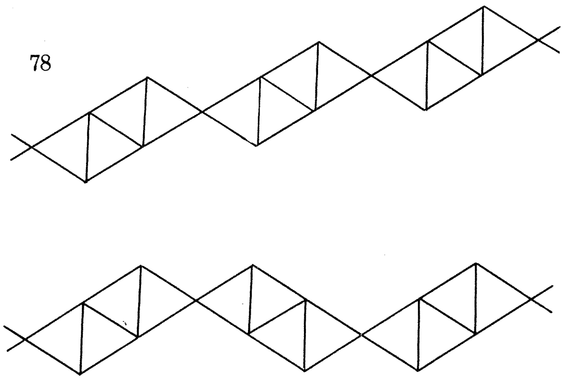

FIGURE 77. Projection of 3D A_2X_5 structure of class III (a_2).
FIGURE 78. Elevations of A_2X_5 layers of class III (b).

TABLE 9. RELATED AX_3 AND A_2X_5 STRUCTURES

AX_3 structure of class III	figure	A_2X_5 structure of class III	
MoO_3 layer	67 }	a_1	idealized V_2O_5
AX_3 layer	68 }		
Th(TiO_6) layer	69	a_2	3D structure (figure 77)
double layers	70 }	b }	3D structures
	71 }		
double layer	72 }		layers (figure 78)

projections of the structures are the same as those of the double layers. There is an indefinitely large number of configurations of the A_2X_5 layer formed from double edge-sharing ('rutile') chains, the two simplest of which are illustrated in figure 78.

Structures of class IV: $v_2 = 4$, $v_4 = 2$

There are two possible arrangements of the two kinds of vertex, namely, *trans* and *cis* arrangements of the two v_4 vertices. Structures have been found only for the latter arrangement. The double (edge-sharing) chain of figure 53 may be joined to two other similar chains to form either a quadruple chain or a layer, by sharing one of the v_1 vertices of each octahedron, the composition becoming AX_3. Sharing of both v_1 vertices of each octahedron gives a layer of composition A_2X_5. Figure 79 shows on the left the projection of this layer and at the right two elevations. There is, therefore, a family of related structures in which each octahedron shares three (equatorial) edges (table 10). Double face-sharing AX_3 chains formed from two rutile chains of which each octahedron shares one face give rise to two structures which are not illustrated because they project as the AX_4 structures of figure 35*b* and *c*. If the pairs of octahedra in these illustrations represent double face-sharing chains perpendicular to the plane of the paper, the A_2X_5 structures are seen to be respectively corrugated layers, of which the simplest is (*b*), and tubular chains (*c*). As in the AX_4 structures, the rings in these tubular chains are restricted to those consisting of 6, 8, 10, or 12 octahedra because of contacts between X atoms of different octahedra.

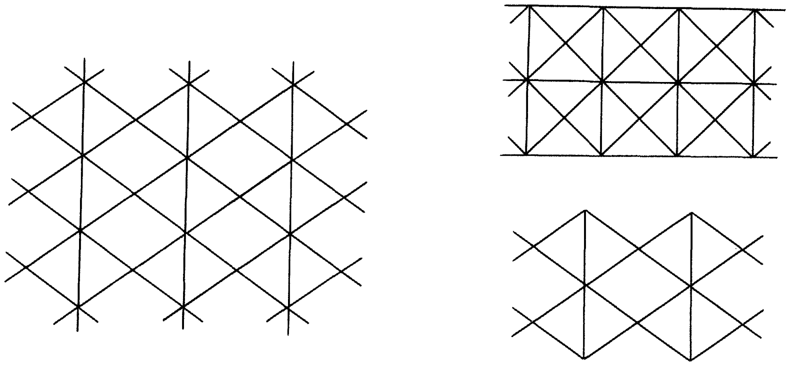

FIGURE 79. Plan and elevations of A_2X_5 double layer of class IV in which each octahedron shares three edges.

TABLE 10. RELATED A_2X_7, AX_3 AND A_2X_5 STRUCTURES

v_1	v_2	v_4	structure	figure
2	2	2	A_2X_7 double chain	53
1	3	2	AX_3 fourfold chain	54
			AX_3 layer	54
—	4	2	A_2X_5 layer	79

The AX_3 (ZrI_3) chains formed from octahedra sharing opposite faces may be joined laterally by sharing edges to produce the double A_2X_5 chain of figure 80. Continuation of this process leads to a corrugated layer of composition AX_2 (table 11).

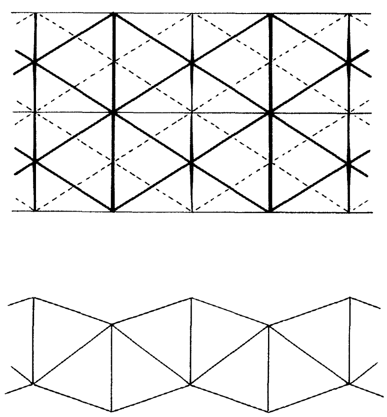

FIGURE 80. Double chain A_2X_5 of class IV formed from face-sharing AX_3 chains.

TABLE 11. RELATED AX_3, A_2X_5 AND AX_2 STRUCTURES

	v_2	v_4	
ZrI_3 chain	6	—	AX_3
double chain	4	2	A_2X_5
layer	2	4	AX_2

Octahedral structures AX_2

We have here to examine five classes (table 1), of which the first includes most of the known AX_2 structures built from octahedral AX_6 groups.

Structures of class I: $v_3 = 6$

As three octahedra meet at each vertex there must be sharing of one or more edges of each octahedron, and it is convenient to list the more important structures as in table 12.

The essential features of the first two structures may be deduced directly from the reasonable requirement that the distance between any pair of X atoms belonging to different octahedra may not be less than the octahedron edge length. It follows that if three octahedra meet at a point (v_3 vertex) there must be at least one edge shared and the edge-sharing pair of octahedra is a rigid unit with $A\genfrac{}{}{0pt}{}{X}{X}A$ coplanar. The position of the third octahedron may range between the positions outlined by the full and broken lines in figure 81*a*, either of which corresponds

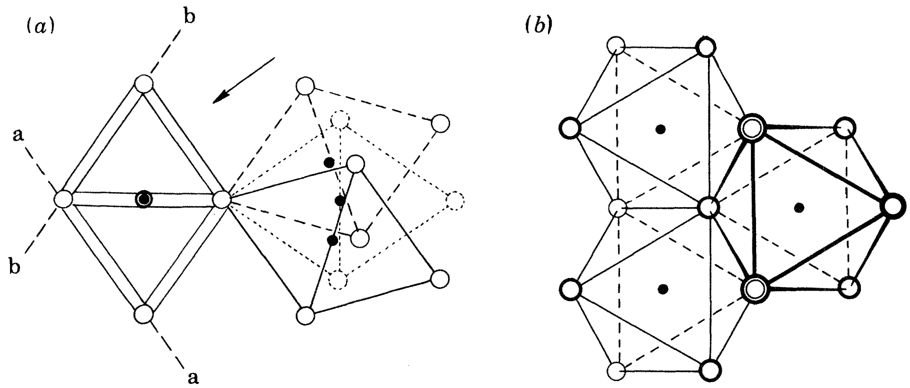

Figure 81. Three octahedra meeting at a point. In (*a*) the two edge-sharing octahedra are seen end-on; in (*b*) the octahedra are viewed in the direction of the arrow in (*a*).

Table 12. AX_2 structures of class I

structure	number of shared edges meeting at each vertex	number of edges shared by each octahedron	edges shared (figure 82)	packing of X atoms
rutile-$CaCl_2$	1	2 opposite	(*a*)	h.c.p.
α-PbO_2	1	2 skew	(*b*)	h.c.p.
anatase	2	4	(*c*)	c.c.p.
atacamite	3	6	(*d*)	c.c.p.
$CdCl_2$	3	6	(*e*)	c.c.p.
CdI_2	3	6	(*e*)	h.c.p.
figure 84*a*	1 and 3 (equal numbers)	4	(*f*)	h.c.p.

to h.c.p. X atoms, the c.p. layers being perpendicular to the plane of the paper and intersecting it in the lines aa or bb. Either of these arrangements corresponds to the h.c.p. $CaCl_2$ structure, with ideal bond angles at X of 90° and 132° (two). The intermediate position shown by the dotted lines represents the situation in the tetragonal rutile structure, in which X has three coplanar A neighbours and ideal bond angles of 90° and 135° (two). Figure 81*b* shows the three octahedra drawn with full lines in (*a*) viewed in the direction of the arrow, that is, projected on a c.p. layer. In an AX_2 structure constructed from equivalent octahedra, the number of edges *shared by each octahedron* is equal to twice the number of *shared edges meeting at each vertex*. (If each octahedron shares n edges, the total number of shared edges in an assembly of a large number N of octahedra is $\frac{1}{2}Nn$, for each edge is common to two octahedra. The number of vertices (X atoms) is $2N$, and if m shared edges meet at each vertex the total number of shared edges is $\frac{1}{2}(2Nm)$, because each edge joins two X atoms. Hence $\frac{1}{2}Nn = Nm$, or $n = 2m$.) In the simplest structure, with one shared edge at each vertex, each octahedron therefore shares two edges which must have no vertex in common, that is, they must be either opposite or skew edges. These structures are the rutile-$CaCl_2$ and α-PbO_2 (niobite) structures, both h.c.p., which may be built from chains of octahedra sharing opposite or skew edges. The sharing of additional edges gives the structures listed in table 12; the edges shared by each octahedron are shown in figure 82. We do not illustrate the more familiar structures of table 12. The derivation of

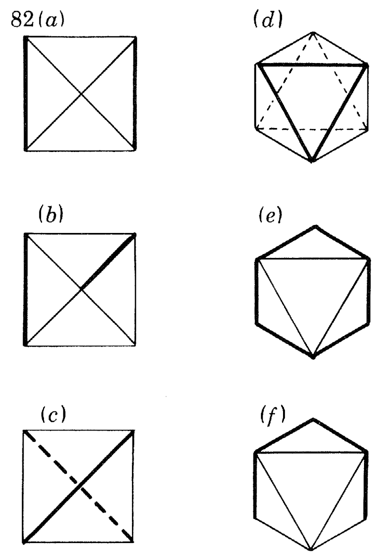

FIGURE 82. The heavy lines indicate the edges of each octahedron shared in the AX_2 structures of table 12.

the anatase structure from skew chains was illustrated in figure 57. The atacamite structure (the idealized structure of the mineral atacamite, $Cu_2(OH)_3Cl$) may be derived by removing the appropriate rows of A atoms from the most symmetrical octahedral AX structure (NaCl) or by stacking the double layers of figure 71 in the way shown diagrammatically in figure 83. The stacking of such layers directly above one another gives the class II structure noted later.

The last entry in table 12 is one of a family of structures built from double rutile chains (figure 72) and represents the structure of α-AlO . OH. All the octahedra are equivalent, sharing the edges of figure 82*f*, but the vertices are of two kinds, at which either one or three shared edges meet. The structure of figure 84*b* is the 3D $Eu_2^{III}O_4$ framework of $Eu^{II}Eu_2^{III}O_4$ or the Fe_2O_4 framework of $CaFe_2O_4$, while figure 84*c* represents the α-MnO_2 (hollandite) structure.

Structures of class II: $v_2 = 2$, $v_4 = 4$

There are two subgroups in this class corresponding to (*a*) *trans* or (*b*) *cis* arrangement of the two v_2 vertices. It is not necessary to illustrate all of the structures in this class because many of them may be formed in obvious ways from structures already described by further vertex- or edge-sharing.

83

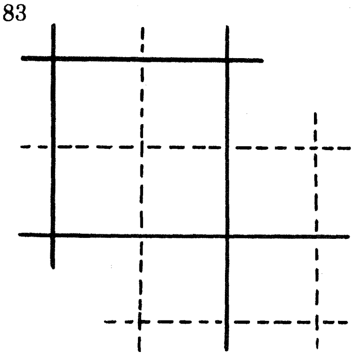

FIGURE 83. The 3D AX_2 (atacamite) structure formed by stacking the double AX_3 layers of figure 71. The full and broken lines represent edge-sharing (rutile) chains.

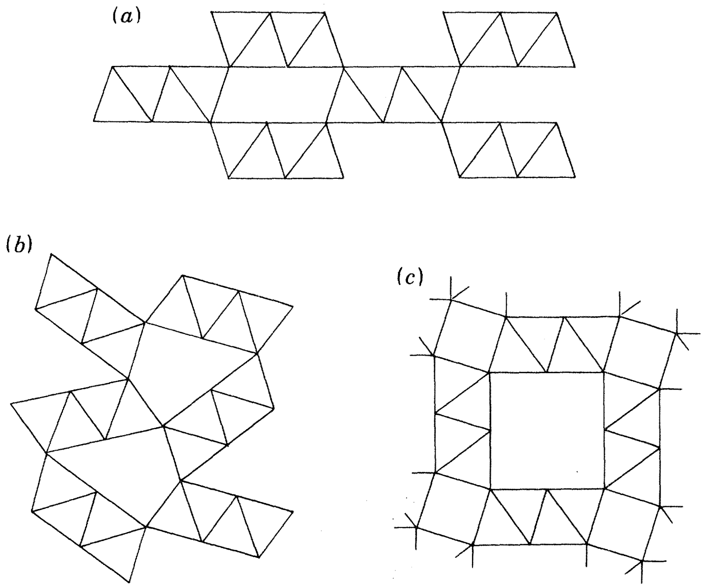

FIGURE 84. AX_2 frameworks of class I built from double edge-sharing rutile chains.

Subgroup (a). Sharing of edges between two parallel ZrI_3 chains gives the double A_2X_5 chain of figure 80. Continued sharing of edges in this way leads to a corrugated layer of composition AX_2 in which each octahedron shares two opposite edges and two opposite faces. In figure 63 we showed three layers in which each octahedron shares one vertex, one edge, and one face, and all vertices are two-connected. Stacking of these layers by sharing two or more edges of each octahedron (those connecting the double circles) converts these vertices into v_4 vertices. The 3D frameworks so formed project as the layers of figure 63. Figure 65 shows the AX_3 layer ($v_1 = 2$, $v_4 = 4$) formed from octahedra sharing four equatorial edges. The same figure represents the projection of the 3D AX_2 structure formed by stacking such layers above one another, when the v_1 vertices become v_2 vertices.

Subgroup (b). Structures extending indefinitely in one, two, or three dimensions are possible in this subgroup. A column of rings of six octahedra stacked face-to-face may be described as a tubular AX_2 chain. The double chain formed from two ZrI_3 chains by edge-sharing was illustrated in figure 80. The corresponding layer belongs to subgroup (a), having *trans* v_2 vertices. This layer could alternatively be described as built of rutile chains running in a direction at right-angles to the face-sharing chains. There is a closely related layer built from *skew* edge-sharing chains. This layer (figure 85), belongs to subgroup (b), having *cis* v_2 vertices. Another layer in this subgroup is that of FeOCl, γ-FeO . OH, and the anion in $Rb_x(Mn_xTi_{2-x}O_4)$ (figure 86). Two 3D structures project as the double layers of figures 70 and 71. These structures are perhaps most easily visualized as formed from the AX_3 chain of figure 66, the chains being set up normal to the plane of the paper and joined by sharing lateral vertices or edges.

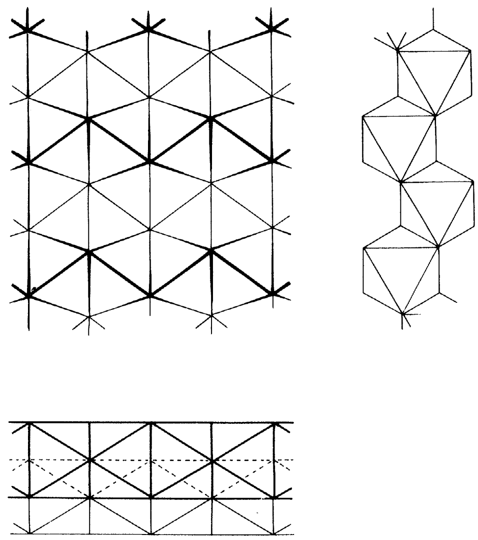

FIGURE 85. AX_2 layer of class II (b).

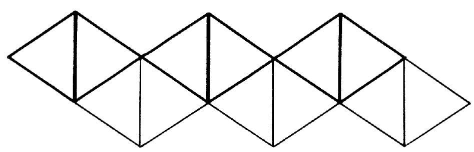

FIGURE 86. Elevation of AX_2 layer of class II (b).

Structures of class III: $v_1 = 1$, $v_5 = 5$

The only structure so far found in this class is the double layer of figure 87. The two side views of the layer show that it may be built either from vertex-sharing (ReO_3) chains (above) or from edge-sharing (rutile) chains (below). In this structure each octahedron shares eight edges.

Structures of class IV: $v_2 = 1$, $v_3 = 3$, $v_4 = 2$

As in class II A_2X_5, the arrangements of the three kinds of vertex correspond to the isomers of an octahedral complex Mab_2c_3 (figure 49), the black circles representing v_3 and the open circles v_4 vertices. The structures we have found are all of the type of figure 49*c*. They are formed from double edge-sharing chains (figure 88) and from double face-sharing rutile chains (figure 89). Examples of these 3D frameworks appear to be confined to the anion framework of $CaTi_2O_4$ (figure 88*b*) and to the structure of γ-$Cd(OH)_2$ (figure 89*a*).

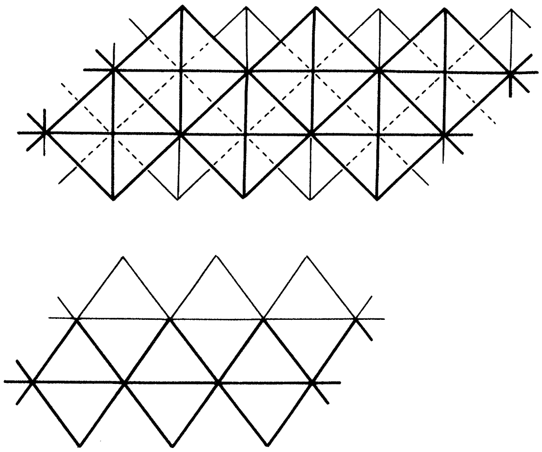

FIGURE 87. Two side views of AX_2 layer of class III.

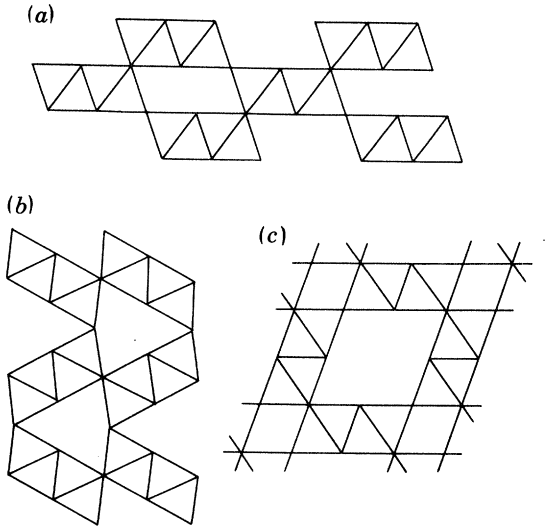

FIGURE 88. Projections of 3D AX_2 structures of class IV formed from edge-sharing double rutile chains perpendicular to the plane of the paper.

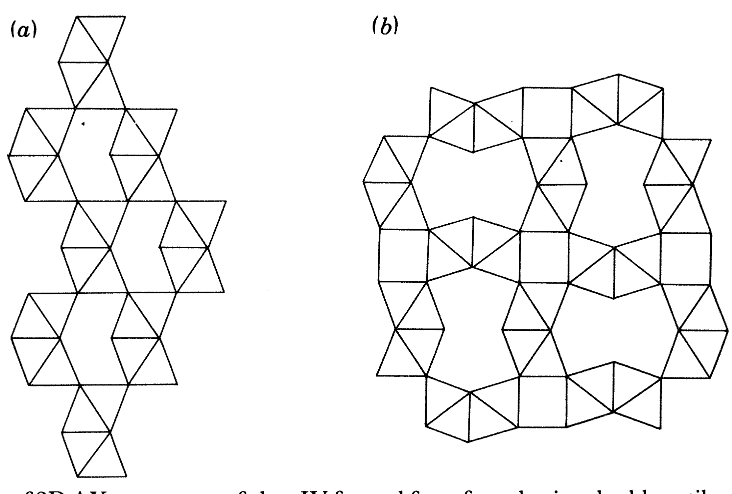

FIGURE 89. Projections of 3D AX_2 structures of class IV formed from face-sharing double rutile chains perpendicular to the plane of the paper.

Structures of class V: $v_2 = 2$, $v_3 = 1$, $v_6 = 1$

The only example found of a structure of this class is the $CdCl_2$-like layer built of 'super-octahedra' A_6X_{19}.

Octahedral structures A_2X_3

Structures have been found corresponding to four of the seven solutions of table 1. These structures may be derived from the h.c.p. or c.c.p. AX structures (NiAs or NaCl structures) in various ways.

Structures of class I: $v_4 = 6$

Three structures in which all octahedra are equivalent may be built from the $AX_3(AlCl_3)$ layer of figure 58, the layers being stacked so as to maintain hexagonal or cubic closest packing of the X atoms. The simplest h.c.p. structure projects as figure 58, and results from removing rows of A atoms parallel to [0001] from the NiAs structure. As in that structure each octahedron shares two faces. The coordination group of every X atom is that corresponding to (*a*) in figure 3. If adjacent layers are related by a glide plane instead of a mirror plane (figure 90), one half

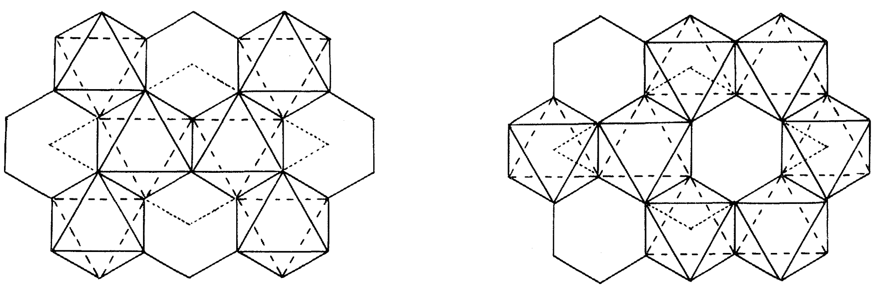

FIGURE 90. Adjacent edge-sharing AX_3 layers in the corundum structure related by a glide plane.

of the octahedra of each layer fall above empty spaces of the layer below, and in the resulting 3D structure each octahedron shares one face. The coordination group of every X atom is of type (*c*) in figure 3; this is the corundum structure. Stacking of the AX_3 layers to give cubic closest packing of the X atoms and maintaining the same translation of adjacent layers gives the structure of figure 91, which is alternatively derived by removing one-third of the A atoms from the NaCl structure in rows parallel to one set of [110] axes. In this structure there are equal numbers of X atoms with the coordination groups (*b*) and (*d*) of figure 3.

Examination of models of the groups of four octahedra of figure 3 shows that for the arrangement (*c*) the environment of X most closely approximates to the ideal for an ionic crystal (regular tetrahedral). The arrangement (*e*) is nearly as favourable, but there does not appear to be a c.p. structure in which all X atoms would have coordination of this type. We might mention here that the simplest alternative to occupying two-thirds of the metal positions between each pair of c.p. layers (the pattern of sites of figure 58 or figure 90) is to have alternately all and one-third of these positions occupied between successive pairs of c.p. X layers. The pattern of *vacant* metal sites in alternate layers of metal atoms is then the pattern of *filled* sites in every layer of the corundum structure. The simplest structures of this kind are those

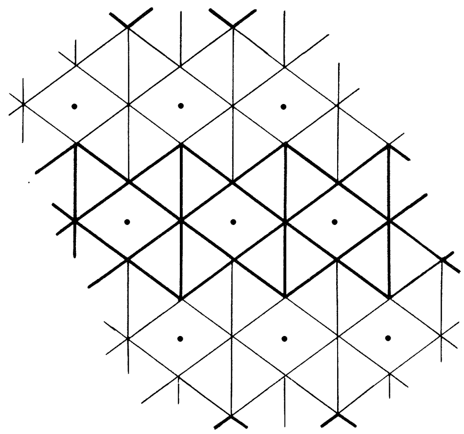

FIGURE 91. The c.c.p. A_2X_3 stucture of class I viewed along a [110] direction which is perpendicular to the plane of the paper. The black dots mark the positions of the rows of missing A atoms.

of trigonal and rhombohedral Cr_2S_3, but in these structures the CrS_6 octahedra share different numbers (0, 1, or 2) of faces.

Structures of class II: $v_3 = 3$, $v_6 = 3$

The two layers illustrated in figure 92 consist of (*a*) a slice of the NiAs structure parallel to (0001), and (*b*) a slice of the NaCl structure parallel to (111). In (*a*) each octahedron shares one face and six edges, while in (*b*) nine edges of each octahedron are shared. The coordination of the six-coordinated X atoms is trigonal prismatic in (*a*) and octahedral in (*b*).

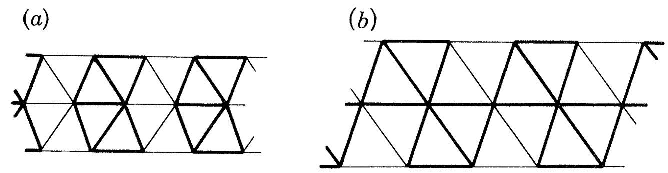

FIGURE 92. Two A_2X_3 layers of class II, perpendicular to the plane of the paper, derived from (*a*) the NiAs, and (*b*) the NaCl structures.

Structures of class III: $v_2 = 1$, $v_5 = 5$

Only one structure has been found in this class: the 3D structure of figure 93. It can obviously be derived from the AX_2 class III structure (figure 87) by joining the double layers to form a 3D structure, the v_1 vertices becoming v_2 vertices. As in the double layer, each octahedron shares eight edges. In this structure there is cubic closest packing of the X atoms, and the structures may alternatively be derived by removing rows of A atoms from the NaCl structure parallel to a set of [110] axes; compare the structure of figure 91, which results from removal of A atoms along a different set of [110] axes. No structure in this class has been found with h.c.p. X atoms.

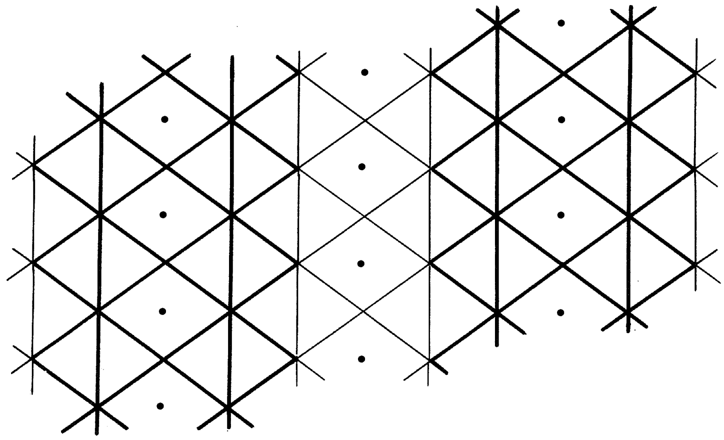

FIGURE 93. The A_2X_3 structure of class III. As in figure 91 the black dots mark the positions of the rows of missing A atoms.

Structures of class IV: $v_2 = 1$, $v_4 = 2$, $v_6 = 3$

Only one structure has been found in this class. It is a corrugated double layer which is a vertical slice of the NiAs structure (figure 94). Each octahedron shares two faces and four edges.

The A_2X_3 structures described above are summarized in table 13. They are separated into two groups corresponding to the packing (h.c.p. or c.c.p.) of the X atoms and arranged in order of decreasing numbers either of shared faces or of edges.

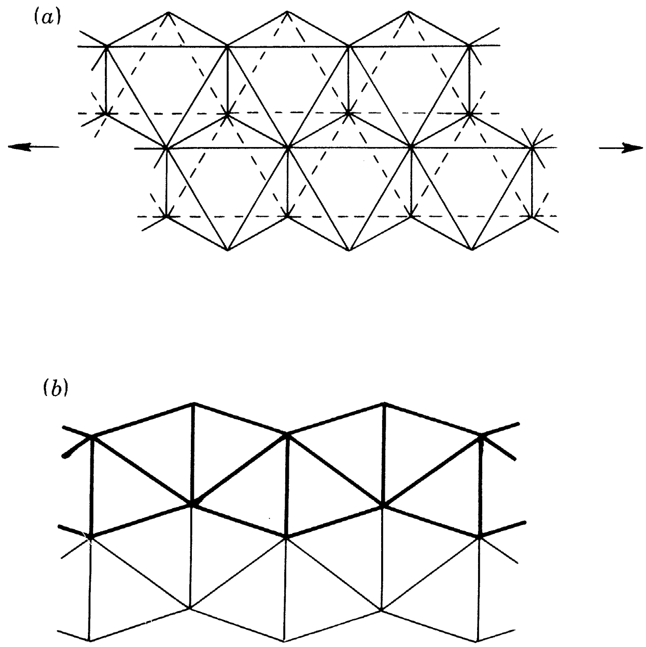

FIGURE 94. The A_2X_3 layer structure of class IV viewed in directions (*a*) perpendicular and (*b*) parallel to the plane of the layer.

Table 13. Summary of A_2X_3 structures

packing of X atoms	number of shared faces	edges	class	figure
h.c.p.	2	3	I	58
	—	4	IV	94
	1	3	I	90
	—	6	II	92*a*
c.c.p.	0	7	I	91
	—	8	III	93
	—	9	II	92*b*

Octahedral structures AX

The two layers of figure 92*a* and *b* are slices of the NiAs and NaCl structures, in which structures the A atoms occupy all the octahedral interstices between layers of hexagonal (*h*) or cubic (*c*) close-packed X atoms respectively. In the NiAs structure the coordination of X is trigonal prismatic, and each octahedron shares six edges and two faces, while in the NaCl structure the coordination of X is octahedral and each octahedron AX_6 shares all twelve edges. A third structure in which all octahedra are equivalent is formed by alternating double layers of types *a* and *b* (figure 92). In this structure there is *hc* packing of X atoms. Each octahedron shares nine edges and one face, and there is trigonal prismatic and octahedral coordination of equal numbers of X atoms.

The packing of X atoms in structures based on the net 10^3-b

In deriving the structures described above we have been concerned only with the ways in which regular octahedra may be joined together to form structures with compositions AX_n or A_2X_n, that is, we have fixed the coordination number of X at 6 and have found the various combinations of c.ns of X that are consistent with the particular formula. We have not discussed the geometrical configurations of the structures; these depend on interbond angles.

No variation in A–X–A bond angle is possible for X atoms belonging to shared edges (A–X–A, 90°) or shared faces (A–X–A, $70\frac{1}{2}$°), but for X atoms shared as separate vertices the angle may range from 180° to 132°. The A–X–A angles are related to the mode of packing of the X atoms, and this aspect of the structures is of interest for the following reason. If the density of packing is less than that of closest packing there is the possibility that it might be increased by rotations of octahedra relative to one another, so increasing the van der Waals contribution to the lattice energy. For example, the X atoms in the ReO_3 structure occupy three-quarters of the positions of cubic closest packing, and Re–O–Re is 180°. Rotation of the octahedra is possible to form a hexagonal closest packed AX_3 structure in which M–X–M is reduced to 132°, as in RhF_3. The point of chemical interest is that there must be a reason for the less dense structure, which in this case is the 'superexchange' through O in ReO_3.

In table 14 are listed seven structures based on the 3D three-connected net 10^3-b in which all shared X atoms are two-connected. In all these structures except that of figure 60 there is sharing of one or more vertices (as opposed to edges or faces), and all of the others except that of figure 47 have been illustrated with collinear A–X–A bonds, that is, in their least dense configurations. The lowest packing density of X atoms is that in the A_2X_9 structure, in which

Table 14. Packing of X atoms in structures based on the net 10^3-b

formula	types of vertices v_1	v_2	octahedra sharing	packing of X atoms	figure
A_2X_9	3	3	3*V* (*mer*)	$\frac{9}{16}$ c.c.p.	6
AX_4	2	4	2*V* 1*E*		
			(class Ic_1)	$\frac{4}{5}$ c.c.p.	19
			(class Ic_2(ii))	$\frac{4}{5}$ c.c.p.	28
A_2X_7	1	5	1*V* 2*E*	$\frac{7}{8}$ c.c.p.	39
			2*V* 1*F*	$\frac{7}{8}$ h.c.p.	47
AX_3	0	6	3*E*	c.c.p.	60
			1*V* 1*E* 1*F*	*hc*	64

there is only vertex-sharing. This structure may be derived from the ReO_3 structure by removing one half of the A atoms and one quarter of the X atoms: $A_4X_{12} - A_2X_3 = A_2X_9$. The packing density of the X atoms is therefore $(\frac{3}{4})^2$ or $\frac{9}{16}$ of that of cubic closest packing. The two AX_4 structures may be derived from the AX_2 structure which projects as figure 65, by removing three fifths of the A atoms and one fifth of the X atoms: $A_5X_{10} - A_3X_2 = A_2X_8$. The A_2X_7 structure of figure 39 is also obviously derivable from the same AX_2 structure.

References

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Wells, A. F. 1983*b* *Acta crystallogr.* B **39**, 652.
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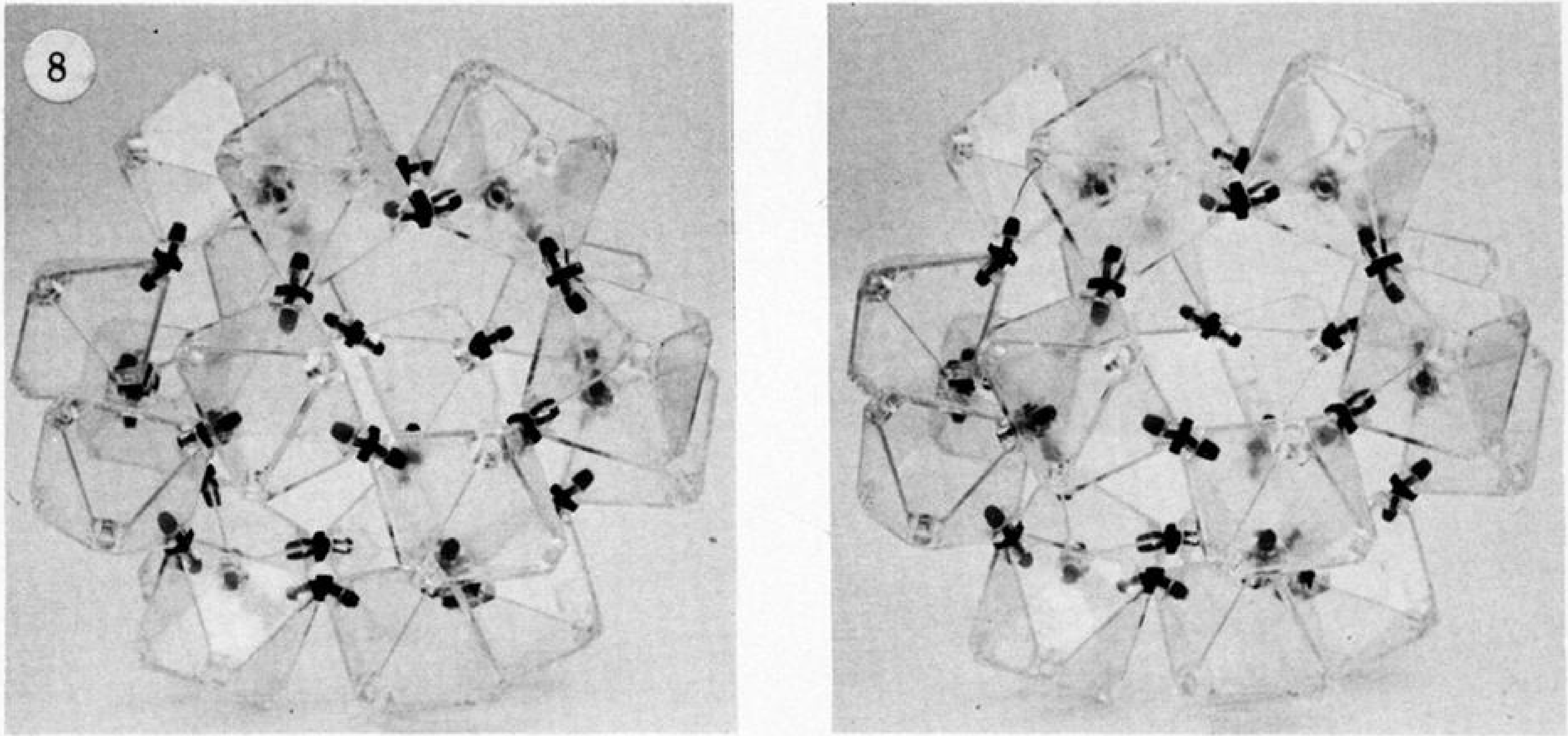

FIGURE 8. The $A_{20}X_{90}$ complex of subgroup a_2. In all stereophotographs of models except figure 14 only *shared* X atoms are shown (as balls or connectors).

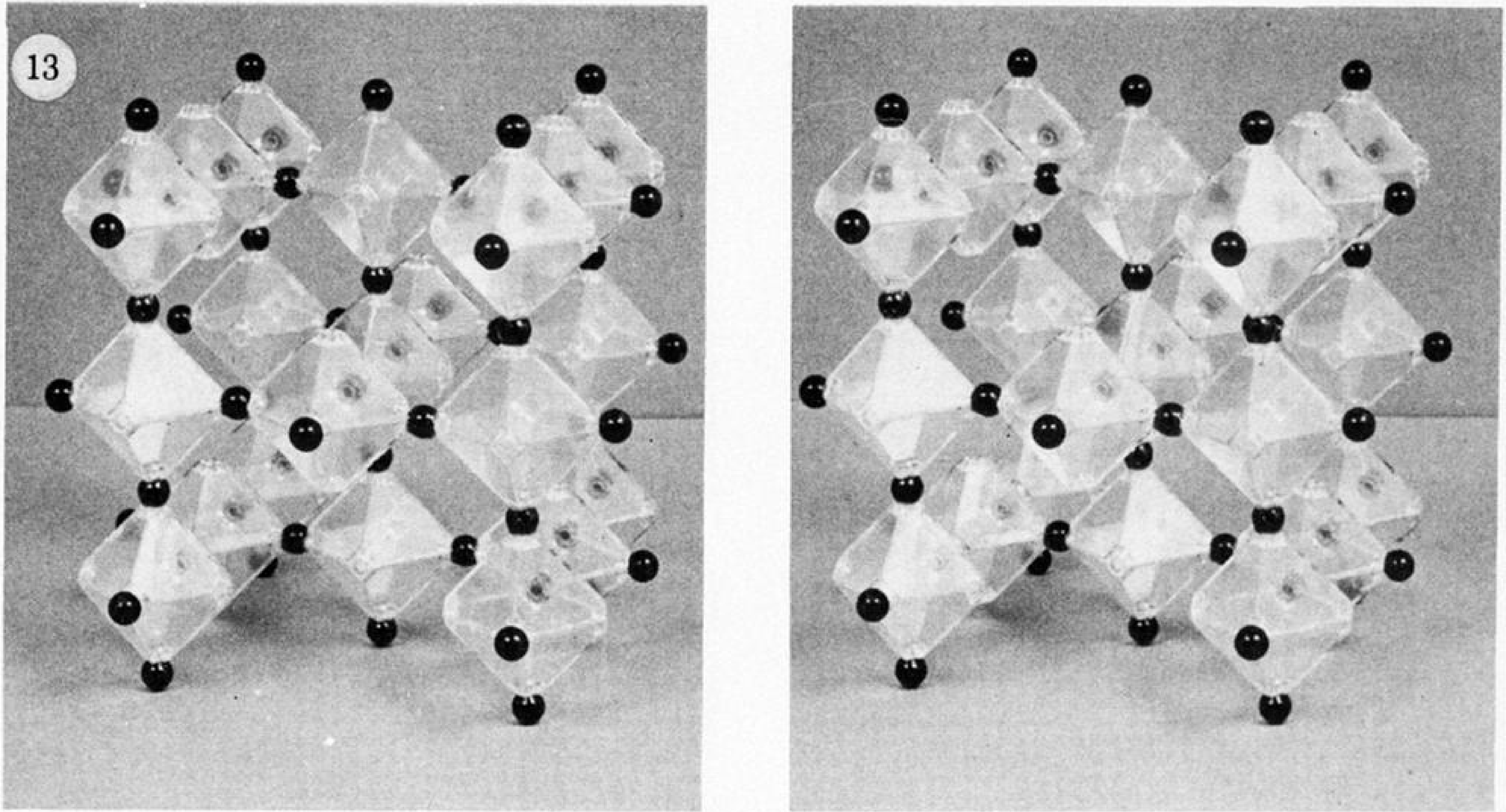

FIGURE 13. Vertex-sharing AX_4 structure of class I (a_1) based on the net $6^4 8^2$.

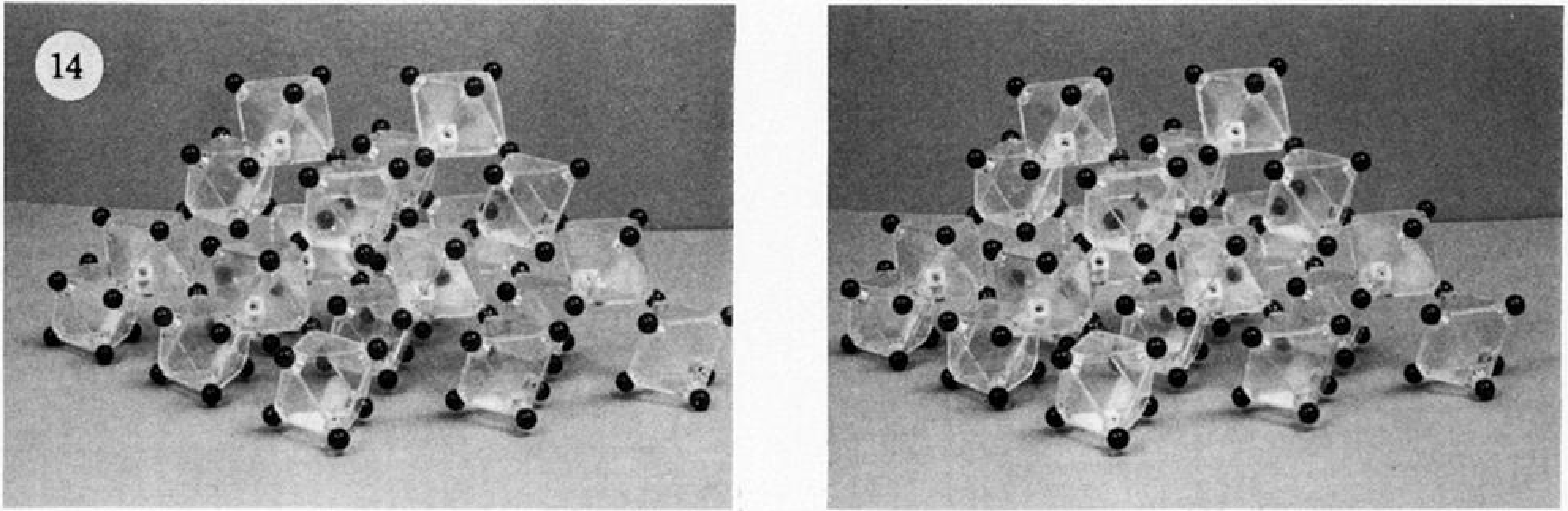

FIGURE 14. The AX_4 structure of class I (a_2) based on the diamond net.

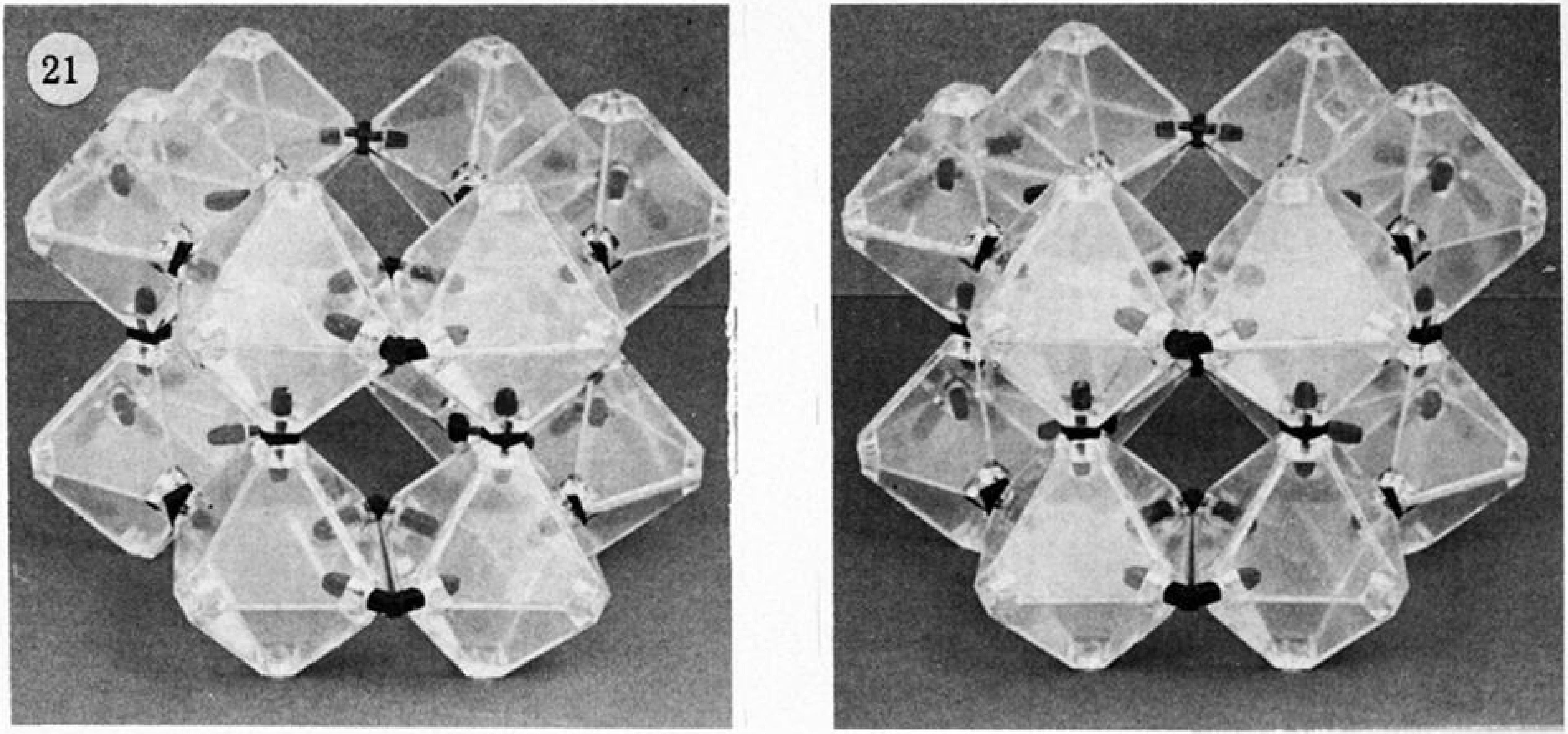

FIGURE 21. Prismatic complex $A_{12}X_{48}$ formed from the sub-unit of figure 20*a*.

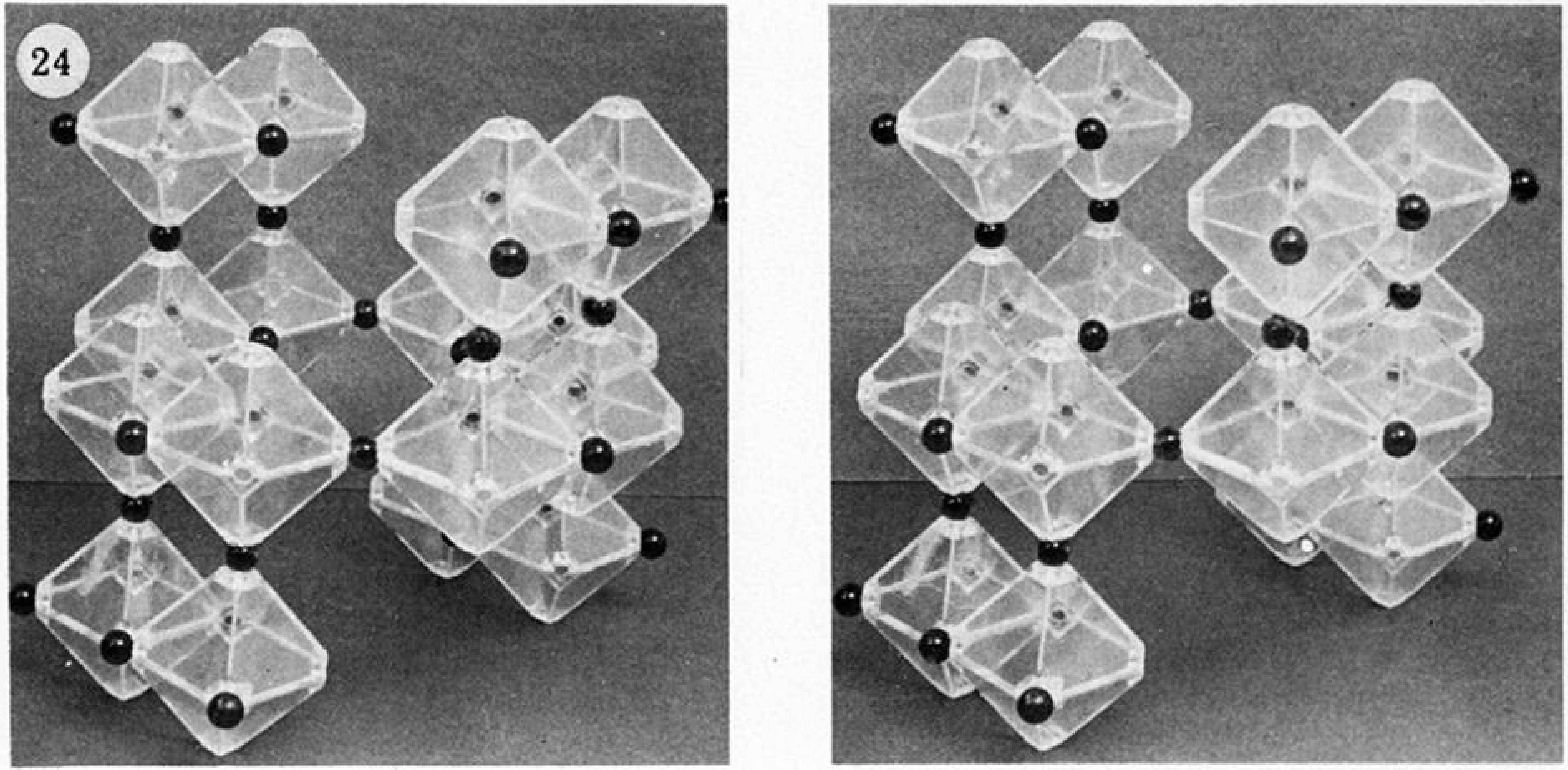

FIGURE 24. Sub-unit of the body-centred structure based on 4.8.10-a formed from the four-octahedron group of figure 20*b*.

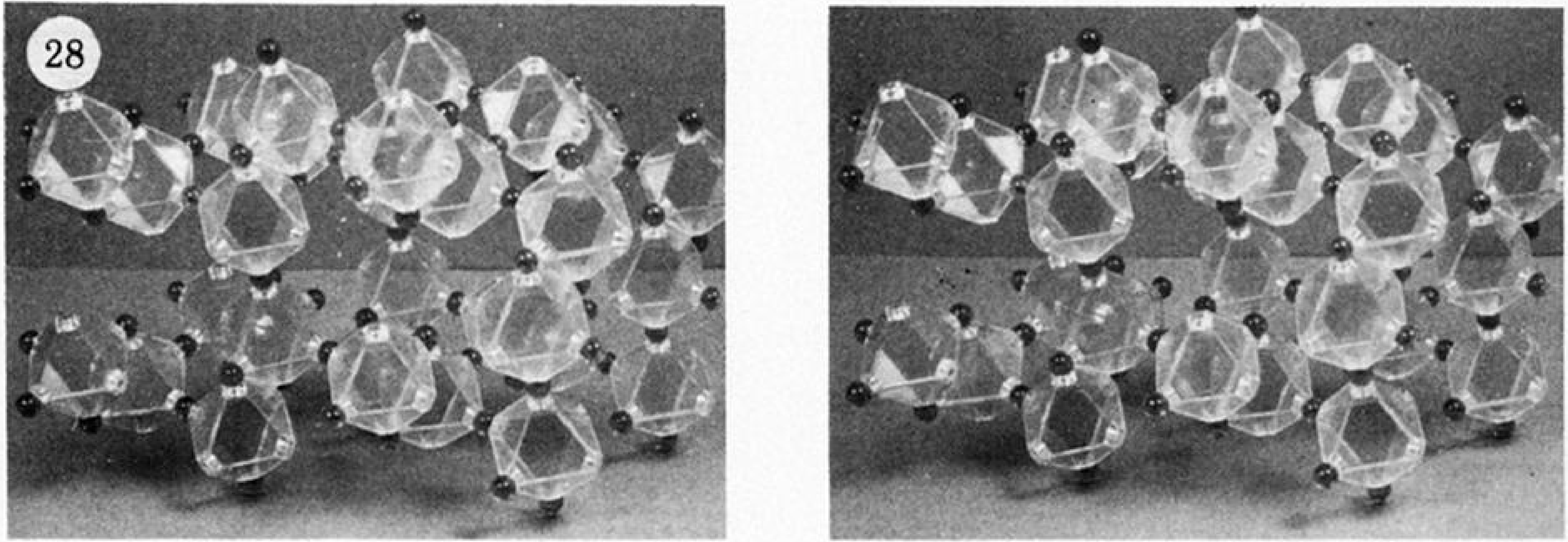

FIGURE 28. AX_4 structure of class I (c_2)(ii) based on the net 10^3-b.

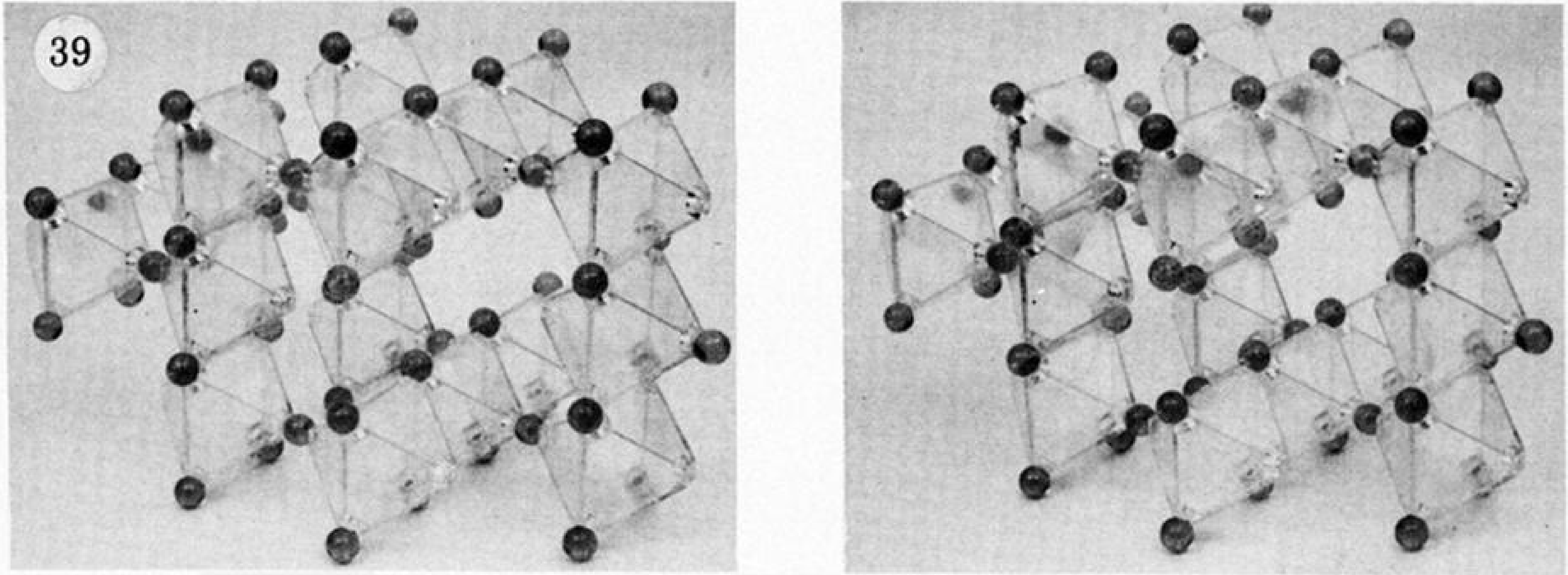

FIGURE 39. A_2X_7 structure based on the net 10^3-b.

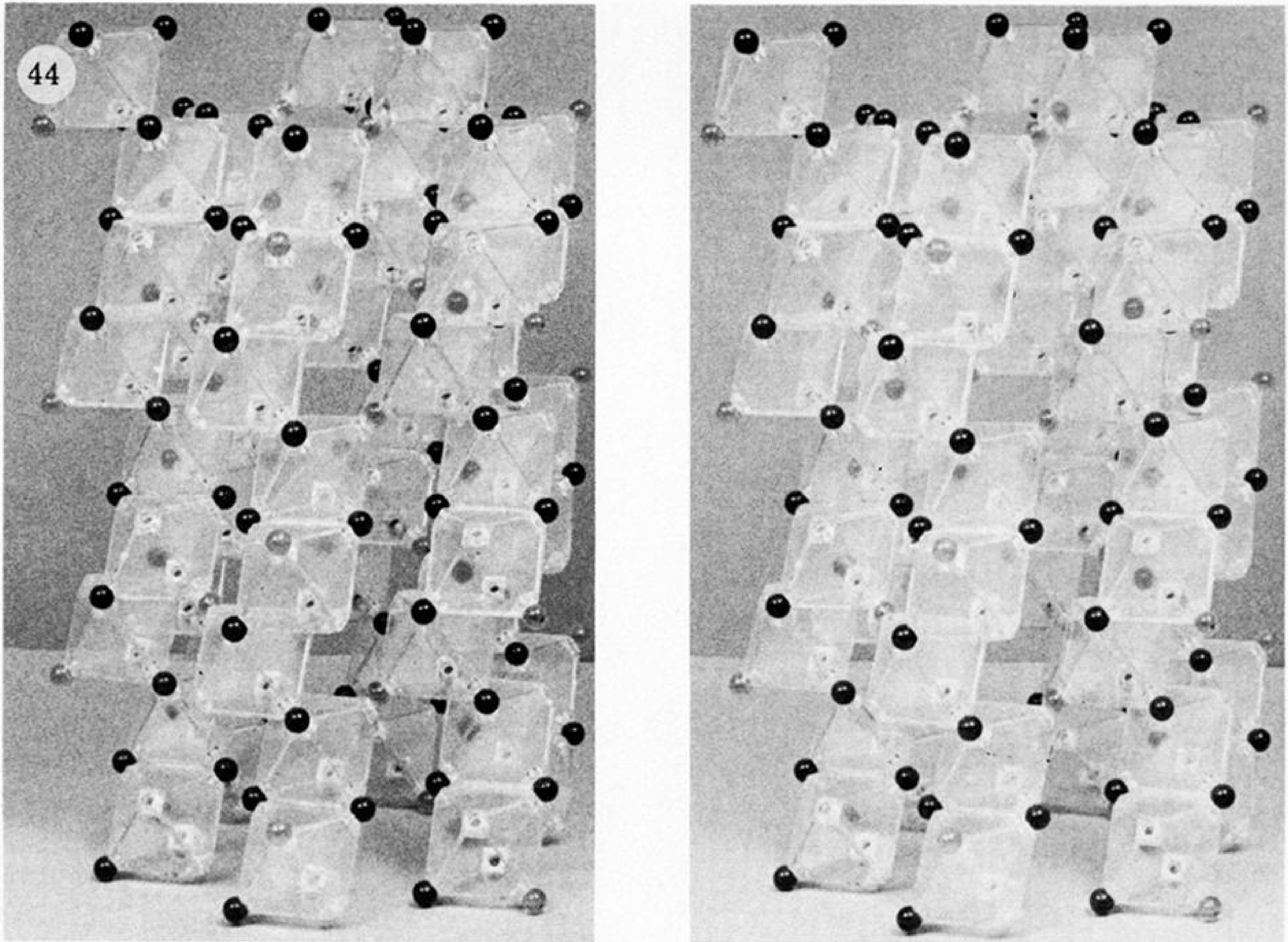

FIGURE 44. Portion of the A_2X_7 structure of figure 43.

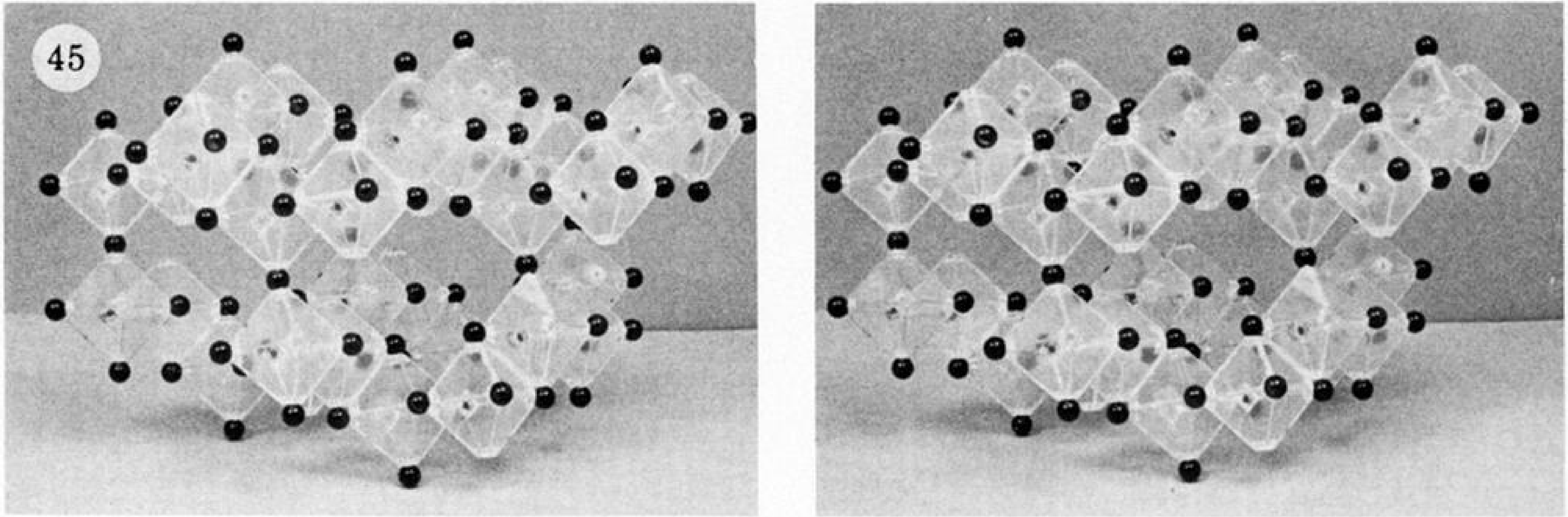

FIGURE 45. A_2X_7 structure of class I (c_2) based on 10^3-a.

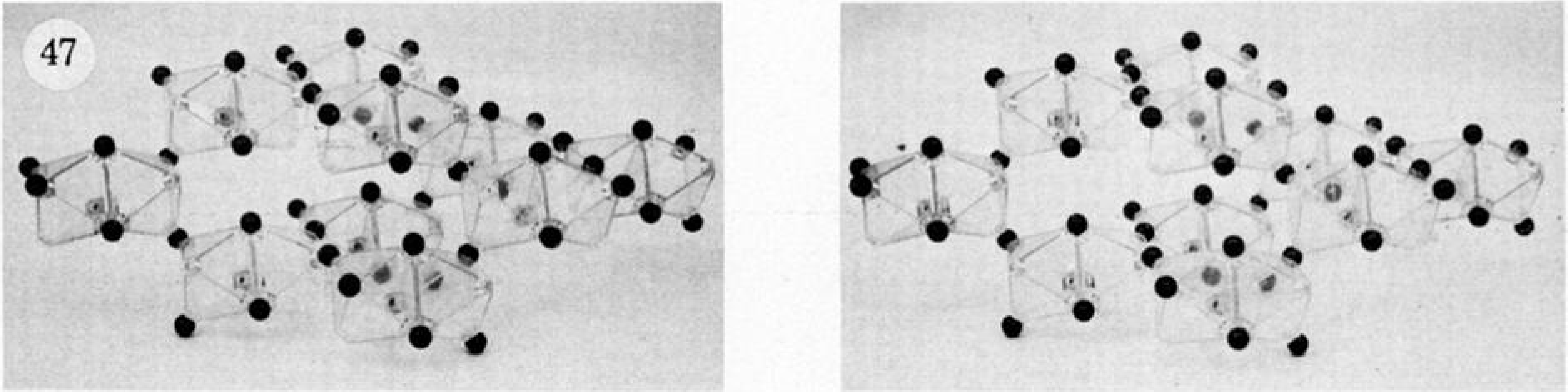

FIGURE 47. A_2X_7 structure of classI (d) based on 10^3-b.

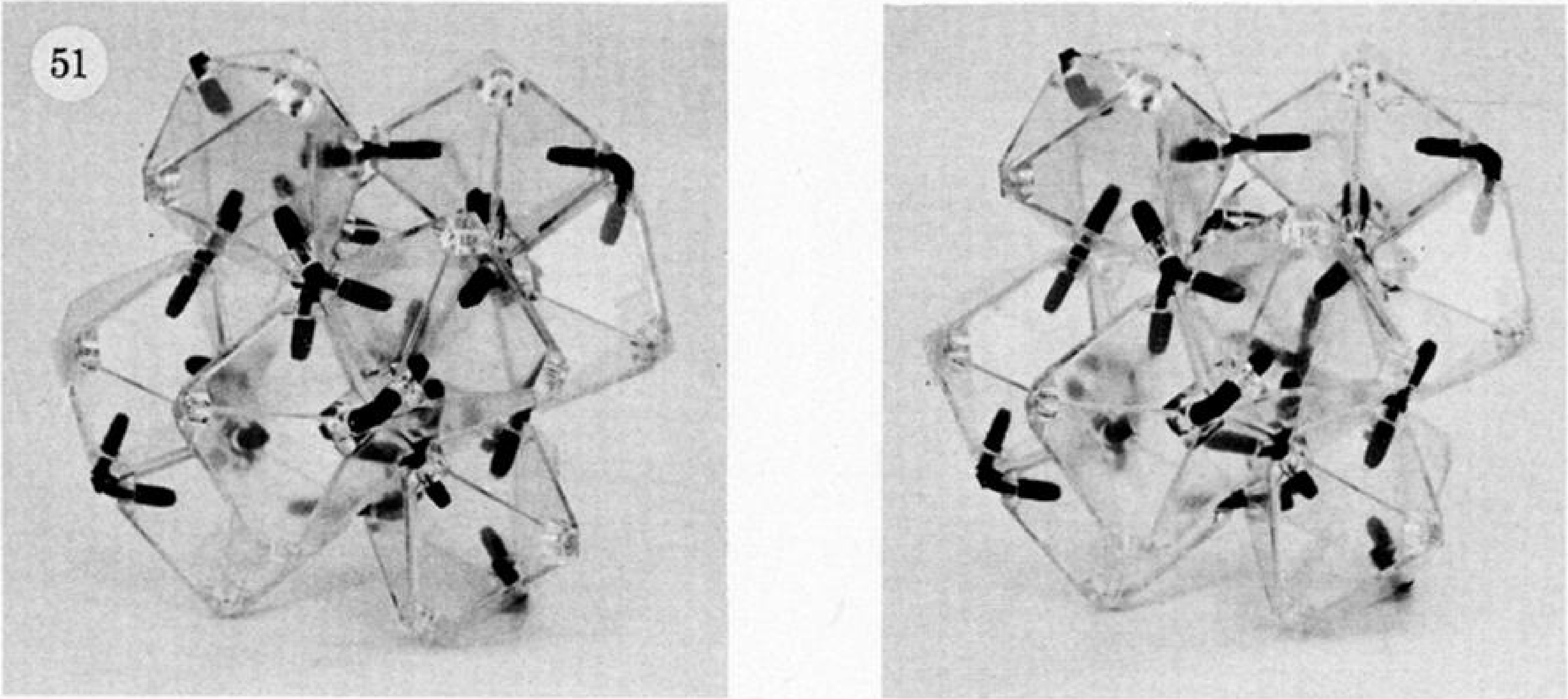

FIGURE 51. The finite $A_{12}X_{42}$ complex of class II (c) based on the icosahedron.

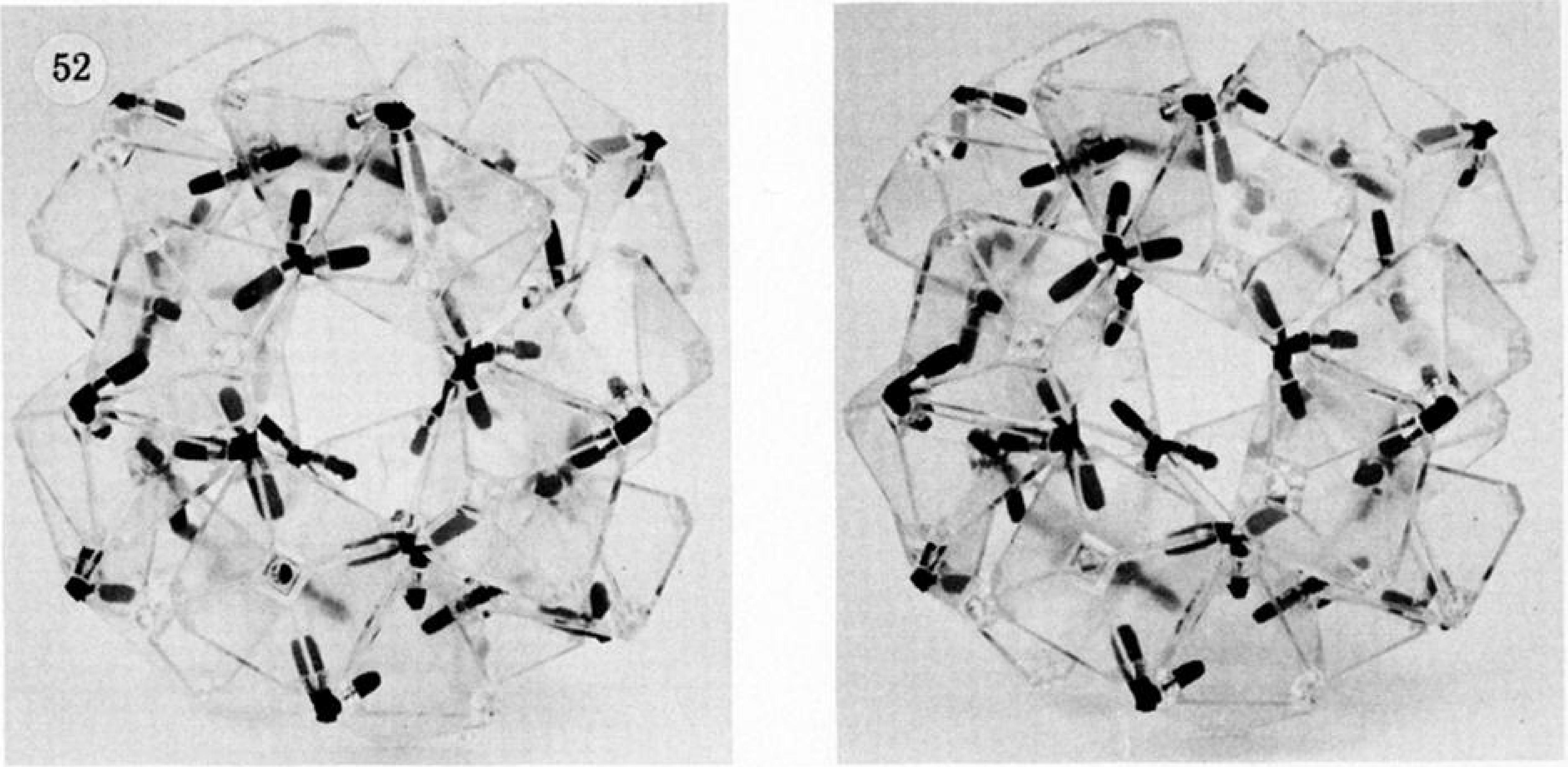

FIGURE 52. The complex $A_{24}X_{84}$ based on the snub cube.

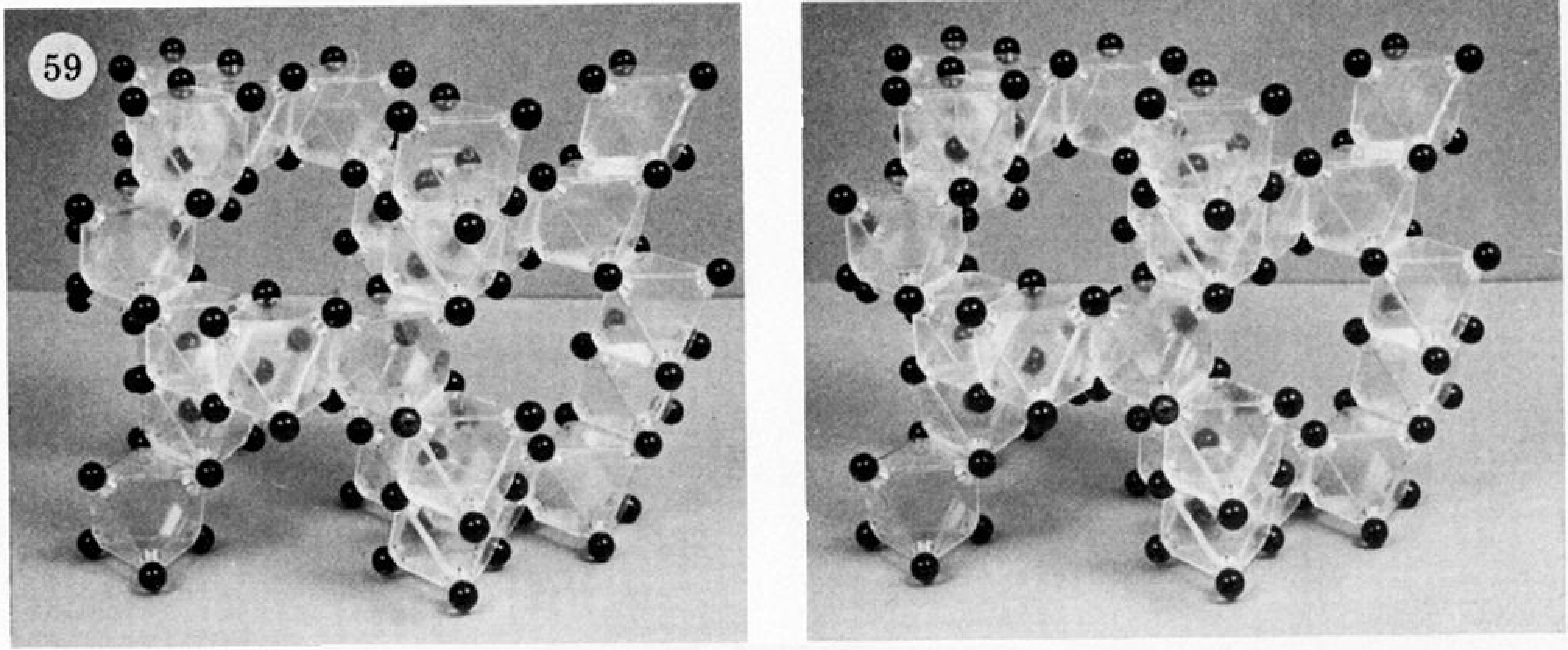

FIGURE 59. AX_3 structure of class I (d) based on 10^3-a.

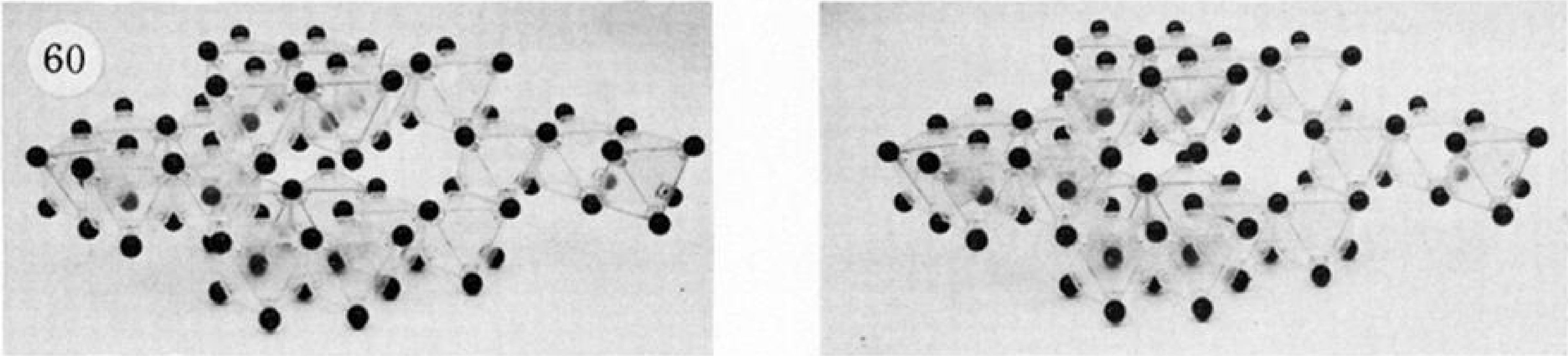

FIGURE 60. AX_3 structure of class I (d) based on 10^3-b.

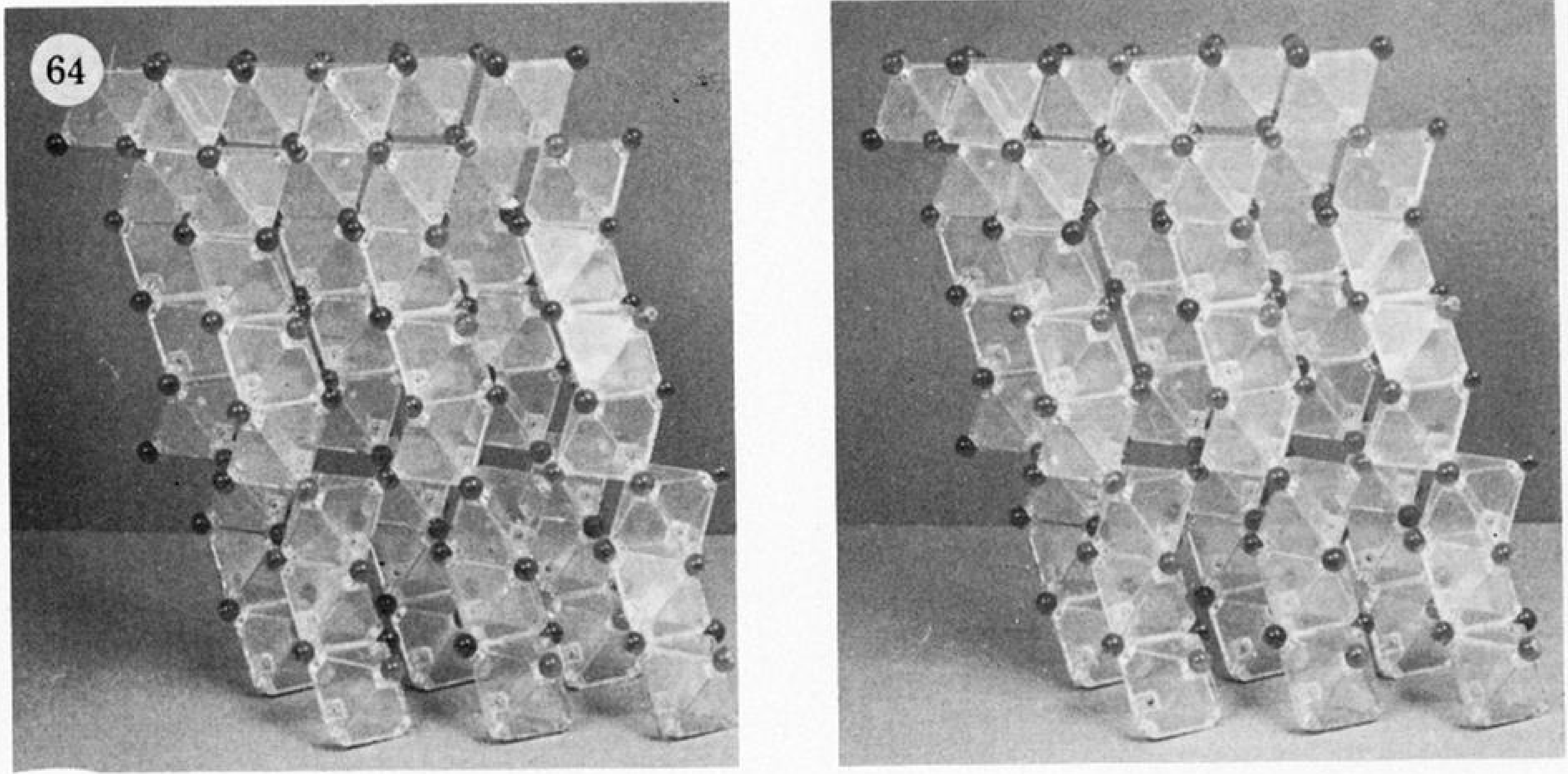

FIGURE 64. AX_3 structure of class I (g) based on 10^3-b.