

The Octahedron in Chemistry

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An investigation is made of some aspects of the geometry of repeating patterns in which various numbers of octahedra meet at each point, and its relevance to the structures of a number of ions, molecules, and crystals is examined. Structures discussed include the rutile and corundum structures. The relation between charge balance and purely geometrical factors in complex oxides and oxy-salts is briefly discussed.

It is the purpose of this paper to state some simple facts about the geometry of the octahedron and to show how they are directly relevant to the structures of crystals and molecules (particularly to generalizations about the sharing of edges and faces of coordination polyhedra), to the discussion of interbond angles, and to questions such as the stability, or indeed existence, of particular groups of compounds and other matters which at first sight are of a purely chemical nature. At a time when "solid state chemistry" and "solid state physics" are being so actively investigated it is regrettable that the study of solid geometry has been replaced in many elementary mathematics curricula by more sophisticated branches of mathematics. Unless his work is directly concerned with the structures of solids, the professional chemist, whether researcher or teacher, still thinks in terms of finite molecules, in spite of the fact that the chemical formulae of even quite simple compounds can only be understood as arising from patterns of atoms which repeat indefinitely in one, two, or three dimensions.

The five regular (Platonic) solids have been known since classical times, but the geometry of systems of polyhedra joined by sharing vertices, edges, and/or faces has received only a limited amount of study. In general the professional mathematician does not concern himself with repeating patterns; instead, the systematic study of extended arrays of points and lines and of the areas or volumes they enclose in ordinary

(Euclidean) space is apparently still considered the province of the crystallographer. Work of outstanding importance in this field includes that of Euler and others on polyhedra and plane patterns, that of Barlow on sphere packings, and the study of space-filling arrangements of polyhedra by Fedorov (similarly oriented polyhedra) and Andreini (combinations of regular and Archimedean semi-regular solids). There is a considerable field of study concerned with the ways in which polyhedra can be linked together by sharing vertices, edges, or faces, or combinations of these elements. Many of the simpler vertex-sharing systems of tetrahedra were encountered as the structures of silicates and aluminosilicates in the early years of X ray crystallography; aspects of this subject which have been studied more recently include the configurations of $(\text{SiO}_3)_n$ chains (1) and $(\text{Si}_2\text{O}_5)_n$ layers (2) and of the 4-connected networks which represent the 3-D frameworks built from tetrahedra sharing all their vertices, as in synthetic zeolites (3). Systematic studies relating to other polyhedra include enumerations of some of the structures formed by octahedra sharing various numbers of vertices, edges, and faces (4), of the linear systems formed from Archimedean antiprisms (5), and of the polyhedral space-fillings which represent the structures of certain groups of transition metal alloys regarded as packings of polyhedral domains (6).

Of the polyhedra encountered in structural inorganic chemistry the octahedron is probably

the most important. Finite octahedral ions AX_6 are relatively unimportant in solution chemistry, but there is an extensive chemistry based on polynuclear oxy and hydroxy ions of elements such as V, Nb, Ta, Mo, W, Te, and I, constructed from octahedral coordination groups. However, the octahedron is of outstanding importance in the structures of solids because (i) the sizes of many metal ions are suitable for octahedral coordination by F^- , O^{2-} , and other halide and chalcogenide ions, (ii) the usual arrangement of six "covalent" bonds is octahedral, and (iii) the interstices in close-packed assemblies of equal spheres are tetrahedral and octahedral interstices. A thorough treatment of the octahedron, including the very numerous one-, two-, and three-dimensional systems that arise by sharing vertices, edges, and faces would cover a large part of structural inorganic chemistry. Such a survey would include many structures in which some of the cations have coordination numbers higher than 6 since there are many crystals in which a framework built from octahedral coordination groups containing a smaller ion enclose larger ions in positions of higher coordination.

It seems likely that there are many "theorems", of a purely geometrical nature, which represent the extension of the usual Euclidean geometry of single polyhedra to systems in which polyhedra are linked together into more complex groupings which may be finite or extend indefinitely in one, two, or three dimensions. It is to be hoped that this type of geometry will one day be recognized, together with the topology of repeating patterns and symmetry, as an integral part of structural chemistry.

Two Octahedra Sharing a Vertex, Edge, or Face

If two regular octahedra AX_6 have a face in common, the angle $A-X-A$ has the value $70^\circ 32'$. If an edge is shared, rotation about the shared edge is possible, but if we insist that the minimum distance between X atoms of different octahedra is not less than the edge length $X-X$ of an octahedron, then the system is invariant with the angle $A-X-A$ equal to 90° . For a pair of vertex-sharing octahedra, with the same restriction ($x \geq l$) the angle $A-X-A$ can range from 180° in the fully extended case to $131^\circ 48'$ at the lower limit (Fig. 1) when $x = l$. (For simplicity we shall use the approximate value 132° for this angle, which is $2 \sin^{-1} \sqrt{5/6}$.)

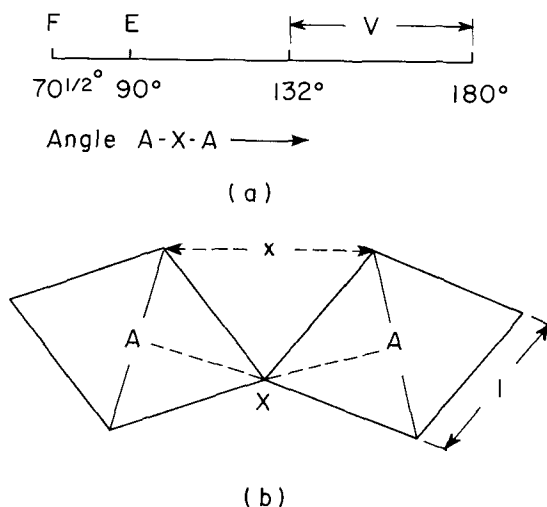


FIG. 1. (a) The possible values of the angle $A-X-A$ for regular octahedra AX_6 sharing a face (F), edge (E), or vertex (V) subject to the restriction, (b), that the distance x between vertices of different octahedra shall not be less than the edge length l .

Each Vertex Common to Two Octahedra only

We examine first the implications of the 132° – 180° range for the $A-X-A$ bond angle in systems in which all octahedra (assumed to be topologically equivalent) share two vertices with other octahedra; this excludes finite systems such as $X_5A-X-AX_5$. Two vertices of an octahedron are either adjacent (*cis*) or opposite (*trans*). Sharing of two *cis* vertices by each octahedron leads to cyclic molecules or zigzag chains [Fig. 2(a) and (b)]. Sharing of *trans* vertices could lead to plane rings of eight or more octahedra (since the octagon is the first regular polygon with an internal angle greater than 132°), but such rings are not known. The alternative is the formation of linear chains [Fig. 2(c)]. The cyclic tetramers M_4F_{20} in crystals of a number of metal pentafluorides are of two kinds, with collinear or nonlinear $M-F-M$ bonds:

F bond angle 180° : $M = \text{Nb, Ta, Mo, W}$

132° : $M = \text{Ru, Os, Rh, Ir, Pt}$.

Other pentafluorides form one or other of the two kinds of chain shown in Fig. 2, and these chains are also the structural units in some oxyhalides and complex fluorides:

cis chain: VF_5 , CrF_5 , TcF_5 , ReF_5 ; MoOF_4 ;
 $\text{K}_2(\text{VO}_2\text{F}_3)$

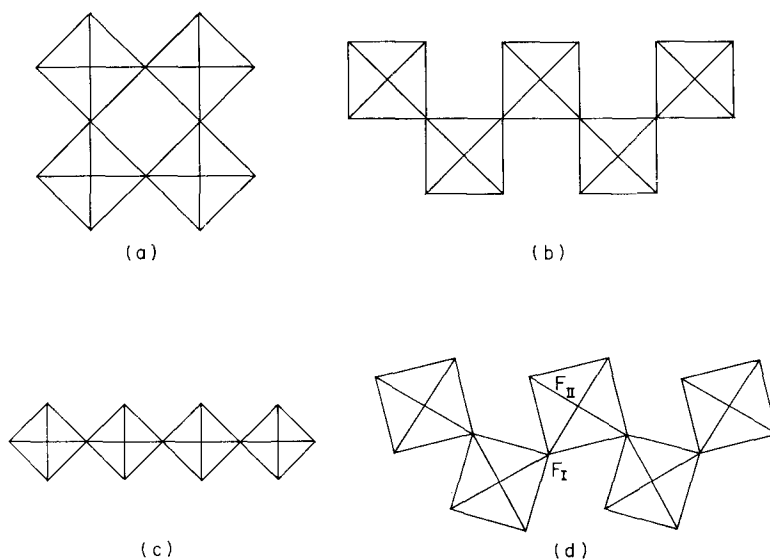


FIG. 2. Octahedra sharing *cis* vertices to form (a) cyclic tetramer, (b) *cis* chain, and (c) sharing two *trans* vertices to form the *trans* chain. (b) and (c) also represent end-on views (elevations) of the *cis* and *trans* layers. (d) The actual configuration of the *cis* layer in BaMnF_4 .

trans chain: BiF_5 , $\alpha\text{-UF}_5$; WOCl_4 ; $\text{Ca}(\text{CrF}_5)$, $\text{Tl}_2(\text{AlF}_5)$.

The factors determining the choice of cyclic tetramer or of one of the two kinds of chain are not understood, and this is true also of the more subtle difference (in $-F-$ bond angle) between the two kinds of tetrameric molecule, a difference which is similar to that between the trifluorides which is noted later.

Corresponding to the two chains formed by sharing two *cis* or *trans* vertices there are layers formed by sharing four vertices, the unshared vertices being *cis* or *trans*. If each square in Fig. 2(b) and (c) represents a chain of vertex-sharing octahedra perpendicular to the plane of the paper, these diagrams are also elevations of the *cis* and *trans* layers. Figure 2(d) shows the elevation of the *cis* layer which is the form of the anion in the isostructural salts BaMF_4 ($M = \text{Mg, Mn, Co, Ni, Zn}$) and in triclinic BiNbO_4 . In this layer (7) there are two types of shared vertex (F atom), F_I and F_{II} , and it is interesting that in the same layer the two $M-F-M$ angles are close to the extreme value of Fig. 1(a), namely, $M-F_I-M$, 139° , and $M-F_{II}-M$, 173° . In the *trans* layer there is sharing of the four equatorial vertices of each octahedron. Examples of neutral molecules with this structure include SnF_4 , PbF_4 , NbF_4 , $\text{Sn}(\text{CH}_3)_2\text{F}_2$, and one form of $\text{UO}_2(\text{OH})_2$. This layer also represents the structure of the two-dimensional anion in

TlAlF_4 and in the K_2NiF_4 structure, which is adopted by numerous complex fluorides and oxides.

The limit of vertex-sharing is reached when each vertex is shared with another octahedron, giving three-dimensional frameworks of composition AX_3 , as in ReO_3 and the tungsten bronzes. The transition metal trifluorides with the ReO_3 and related structures are mentioned later in connection with the corundum structure; like the cyclic pentafluorides they exhibit the $M-F-M$ bond angles in the region of 132° and 180° , but they also exhibit intermediate angles.

Vertex Common to Three or More Octahedra

From the range ($132-180^\circ$) of $A-X-A$ angles it follows that: If more than two regular octahedra meet at a point [that is, share a common vertex (X atom)] they must share one or more edges and/or faces, assuming the condition stated earlier ($x \geq 1$). If three regular octahedra meet at a point, the maximum value of $A-X-A$ is attained when the three A atoms are coplanar, when this angle is 120° . This value falls in the "forbidden" range, between 90° and 132° , and is therefore not possible for regular octahedral coordination groups. In this connection a number of structures are of interest.

(a) *The Ion* $[\text{OCr}_3(\text{OOC}\cdot\text{CH}_3)_6(\text{H}_2\text{O})_3]^+$. In

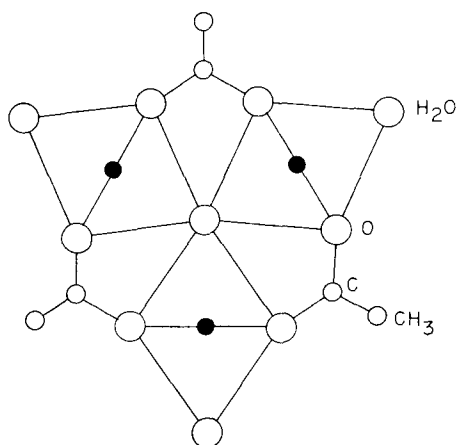


FIG. 3. The ion $[\text{OCr}_3(\text{OOC}\cdot\text{CH}_3)_6(\text{H}_2\text{O})_3]^+$. Two edges of each CrO_6 octahedron are normal to the plane of the paper and are bridged in pairs at their upper and lower ends by $\text{OOC}\cdot\text{CH}_3$ groups, of which only three are shown.

this ion (Fig. 3) three octahedral coordination groups share a common vertex (O atom) but no edges or faces, apparently contradicting the above theorem. Disregarding the (small) departures of the octahedral CrO_6 groups from regularity, this system is possible because it contravenes our requirement that there shall be no van der Waals contacts between vertices of different octahedra closer than those within an octahedron. The acetate groups, in pairs, bridge vertices of different CrO_6 groups, and O-O within the CH_3COO ligands is only 2.24 Å, as compared with the edge length of an octahedron which ranges from 2.63–2.90 Å (8).

(b) *The Rutile Structure.* In a structure of a compound MX_2 with octahedral coordination of M , three octahedral MX_6 groups meet at each X atom. The "ideal" environment of X in an essentially ionic fluoride or oxide would be three coplanar M neighbors at the corners of an equilateral triangle. Since the value 120° for $M-X-M$ lies in the "forbidden" range, such a structure is not possible, and it is necessary to share one edge (at each X atom). These simple geometrical considerations lead directly to the rutile structure (Fig. 4) and would suggest X bond angles of 90° and 135° (two). However, the symmetry (tetragonal) and equivalent positions of the atoms do not define a unique "rutile structure" because there are two variables, namely, the axial ratio $c:a$ and the value of the variable parameter u of the O atom. The number of independent variables reduces to one if all the

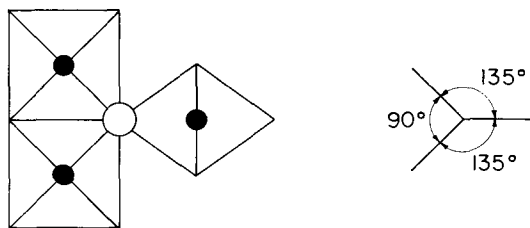


FIG. 4. Three octahedra meeting at a common vertex in the rutile structure.

$M-X$ bond lengths are made equal, when there is the following relation between u and $c:a$:

$$8u = 2 + (c/a)^2.$$

Two special cases are: (i) regular octahedral coordination of M ($c:a = 0.58$, $u = 0.29$), and (ii) equilateral triangular coordination of X ($c:a = 0.817$, $u = 0.33$). Most rutile structures approximate to (i), with $c:a$ close to 0.65 and u close to 0.30.

(c) *The Structures of AgF_2 , PdS_2 , and $\beta\text{-HgO}_2$.* The structures of these three compounds are closely related; all have the same space group ($Pbca$) and the same equivalent positions are occupied, namely, (000) etc. for M and (xyz) for X . All are derived from a hypothetical AX_2 structure in which three octahedra meet at each point without edge- or face-sharing. Since this vertex-sharing AX_2 structure is not possible for regular octahedra it is of interest to see how the octahedra are distorted in different ways in the three structures. The buckled layer of Fig. 5(a) represents a layer of the structure of PdS_2 . If layers (a) and the (inverted and translated) layers (b) alternate in a direction normal to the plane of the paper, an octahedral group $ABCDEF$ around a metal atom can be completed by atoms E and F of layers (b) situated at distances $c/2$ above and below the layer (a). In the resulting three-dimensional structure each X atom is a vertex common to three octahedra, which cannot be regular.

The geometrical difficulty is overcome in one or both of two ways, namely, (i) distortion of the octahedral coordination groups, or (ii) bonding between pairs of X atoms (such as E and F) in each "layer." In AgF_2 there is moderate distortion of the octahedral groups ($\text{Ag}-4\text{F}$, 2.07 Å, $\text{Ag}-2\text{F}$, 2.58 Å) and normal F-F distances between atoms of different coordination groups (shortest F-F, 2.61 Å)—case (i). Fig. 5(c) shows one "layer" of the structure of AgF_2 (9). In

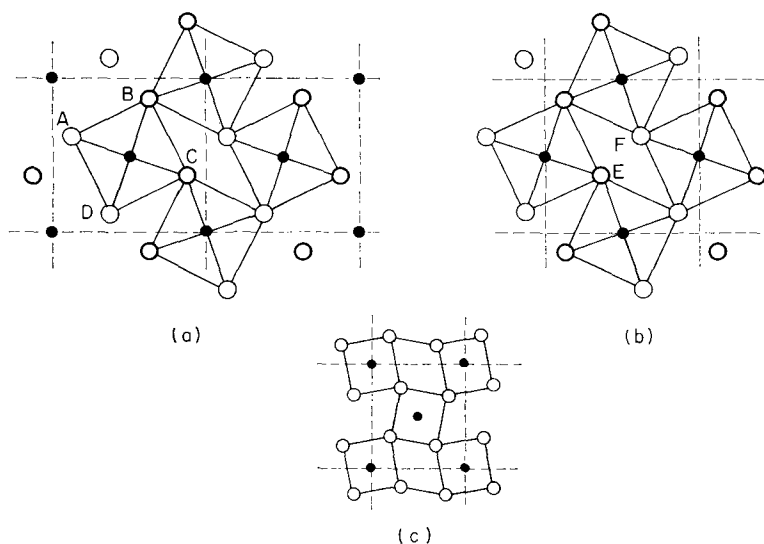


FIG. 5. (a) and (b). Successive "layers" of the structure of PdS₂. (c) One "layer" of the structure of AgF₂.

PdS₂, the S atoms are linked in pairs (S–S, 2.13 Å), and in addition, the octahedral PdS₆ groups are so elongated that the structure is a layer structure (Pd–4S, 2.30 Å, Pd–2S, 3.28 Å). In β-HgO₂ the O atoms are bonded in pairs (O–O, 1.5 Å) and here the octahedra are compressed (Hg–2O, 2.06 Å, Hg–4O, 2.67 Å), so that instead of layers there are chains –Hg–O–O–Hg– in the direction of the *c* axis, normal to the plane of the "layers" in Fig. 5. In these two structures, therefore, both factors (i) and (ii) operate.

M₂X₃ Structures

Octahedral coordination of *M* in a M₂X₃ structure requires that four octahedra meet at (share) every *X* atom, assuming all *X* atoms to be equivalent. Since the value 109½° falls within the "forbidden" region of *M*–*X*–*M* bond angles, a structure with regular octahedral coordination of *M* and regular tetrahedral coordination of *X*, as might be desirable in an essentially ionic oxide M₂O₃, is ruled out. First we may note a much more general restriction, of a topological rather than (geo)metrical nature, on the structures of compounds M₂X₃. We define a simple layer structure for a compound M_{*m*}X_{*n*} as one which can be represented on a plane as a (*p*,*q*)-connected net without *M*–*X* bonds intersecting; this is true for layers such as those in crystalline As₂O₃, CdI₂, FeCl₃, and ThI₄. It can be shown that the only plane (*p*,*q*)-connected nets with alternating *p*- and *q*-connected points (as required for an

oxide or halide) having *p* and *q* ≥ 3 are the (3,4), (3,5), and (3,6) nets. (The case of *p* or *q* equal to 2 is trivial, since 2-connected points may be placed on any line.) Therefore a simple M₂X₃ layer with any type of 6-coordination of *M* is not possible since this could be represented as a (6,4)-connected net; a structure with octahedral coordination of *M* is only a special case of this more general limitation.

The corundum structure. Two structures are commonly found for sesquioxides of octahedrally coordinated ions M³⁺, namely, the *C*-M₂O₃ (Mn₂O₃) and α-Al₂O₃ structures. In both structures there is necessarily distorted octahedral coordination of *M* and/or distorted tetrahedral coordination of O. The *C*-M₂O₃ structure is usually described as approximating to a fluorite-like MO₂ structure from which one-quarter of the anions have been removed, that is, the O²⁻ ions occupy three-quarters of the positions of primitive cubic packing. In the corundum structure the packing of the anions approximates to hexagonal closest packing, and the metal ions occupy two-thirds of the octahedral interstices. The choice of close-packed sequence (and of interstices occupied) is apparently determined by the need to give O²⁻ an arrangement of nearest M³⁺ neighbors approximating as closely as possible to a regular tetrahedral one, necessitating in this case the sharing not only of vertices and edges but also of one face of each AlO₆ coordination group. For this reason the corundum structure is of particular interest in the present

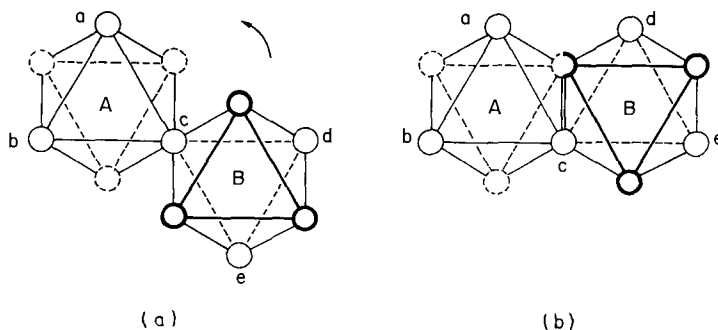


FIG. 6. Relation between vertex-sharing octahedra for the extreme cases (a) angle $A-c-B$, 180° , and (b) angle $A-c-B$, 132° .

connection, but it is also of interest because it (and its superstructures, the ilmenite and LiNbO_3 structures) is related to a number of other structures.

In its fully extended form, with $B-X-B$ bond angles 180° , the three-dimensional framework in which each BX_6 octahedron shares each vertex with one other octahedron is that of ReO_3 (and isostructural trifluorides). The X atoms occupy three-quarters of the positions of cubic closest packing; insertion of a large ion A into the unoccupied positions gives the perovskite structure for compounds ABX_3 which is built of close-packed AX_3 layers. Maintaining the same connections between the vertices of the ReO_6 (BX_6) octahedra the structure may be transformed into the hexagonal close-packed structure (of RhF_3) in which the $M-F-M$ bond angle is reduced to 132° ; intermediate structures are also adopted:

	RhF_3	CoF_3	FeF_3	ReO_3
Angle $M-F-M$	132°	149°	153°	180°

The relation between the two extreme configurations of the vertex-sharing framework is

most easily seen from Fig. 6. The vertices a , b , c , d , and e are in one plane, those shown as dotted circles are below this plane, and those shown as heavy circles are at the same distance above it. Keeping the octahedron A fixed and the vertices a , b , c , d , and e coplanar, rotation of the octahedron B through 60° from the fully extended arrangement (a) ($A-c-B = 180^\circ$) brings it to the position shown at (b) ($A-c-B = 132^\circ$). In (a) the octahedron vertices are in some of the positions of cubic closest packing; in (b) they are in the positions of hexagonal closest packing.

The same octahedral framework as that of RhF_3 represents the arrangement of one-half of the AlO_6 octahedra in corundum; this is more easily seen in LiNbO_3 , where it is the arrangement of LiO_6 or NbO_6 octahedra. This is illustrated by the conventional elevations of these structures in Fig. 7, where that of a perovskite ABX_3 is included. A plot of the $-X-$ bond angle (ranging from 132° to 180°) versus $c:a$ of the hexagonal unit cell (or α of the rhombohedral cell) is a convenient way of showing the geometrical relation between the MX_3 structures of the MO_3

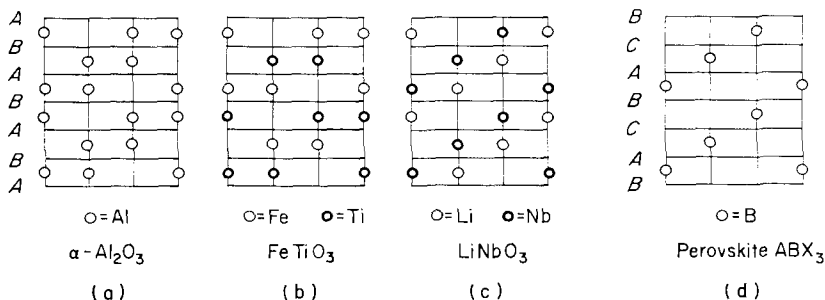
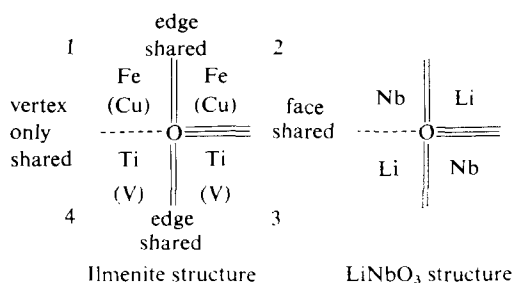


FIG. 7. Elevations of close-packed structures: (a) corundum, (b) FeTiO_3 , (c) LiNbO_3 , (d) perovskite. The letters indicate the sequence of close-packed layers, which in a perovskite ABX_3 are AX_3 layers. The small circles represent metal ions in octahedral interstices between the close-packed layers.

frameworks in the corresponding corundum superstructures, in which $-O-$ is close to the lower limit, and the perovskites, in which $-O-$ is near the upper limit ($160^\circ-180^\circ$). In reference (10), the authors include data for LiNbO_3 and LiTaO_3 but not for any example of the other important corundum superstructure (ilmenite) or for Al_2O_3 itself. It should be noted that in the case of LiNbO_3 and LiTaO_3 it is necessary to specify which $M-O-M$ angle is being discussed. In the corundum structure four octahedra MO_6 meet at each O atom, and pairs of these octahedra are related in different ways according to whether they share a vertex, an edge, or a face. The relative arrangement of the four octahedra must be specified in a discussion of superstructures for it is different in the ilmenite and LiNbO_3 structures:



Either pair of diametrically opposite octahedra in the diagrams share a vertex only and form part of a three-dimensional vertex-sharing array of the MF_3 (ReO_3) type. Table I shows the oxygen bond angles for Al_2O_3 (11) and for LiNbO_3 , omitted from (12) but kindly supplied by Dr. E. Kostiner, who also provided the data for a rhombohedral ilmenite which has been studied

recently (13). The values show very small variations and may be compared with those in the last column of the Table which are the "ideal" values for regular octahedral MO_6 groups noted earlier. These bond angles show appreciable deviations from their mean values, which are $109\frac{1}{2}^\circ$, the value for regular tetrahedral coordination.

Limitations on Numbers of Polyhedra Meeting at a Point

Although a limited number of studies have been made of spacefilling arrangements of polyhedra there appears to have been very little systematic study of the numbers and combinations of polyhedra of various kinds which can meet at a point (that is, share one or more vertices) if the restriction is introduced that the distance between unshared vertices may not fall below a limiting value such as the edge-length, representing a minimum van der Waals distance between non-bonded X atoms. This field of solid geometry is obviously relevant to discussions of the structures of simple compounds A_mX_n , and particularly the nonexistence of structures of high coordination. The occurrence of cubic 8-coordination in CsCl and CaF_2 is undoubtedly due to the impossibility of building three-dimensional structures with the preferred antiprismatic or dodecahedral coordination which is so frequently observed in more complex structures, where there are more degrees of freedom, and in finite ions and molecules, which are not subject to the restrictions associated with repeating patterns. In the series of structures, CsCl , CaF_2 , and UCl_4 , the 8-coordination of the cations implies respectively 8-, 4-, and 2-coordination of the anion, that is,

TABLE I
OXYGEN BOND ANGLES IN CORUNDUM AND SUPERSTRUCTURES

	Octahedral element shared	Al_2O_3	CuVO_3	LiNbO_3	Value for regular octahedra
2-3	Face	85°	Cu-O-V 88°	Li-O-Nb 88°	$70\frac{1}{2}^\circ$
1-2 3-4	} Edge	94°	Cu-O-Cu 87°	Li-O-Nb 94°	90°
			V-O-V 98°	Li-O-Nb 95°	
1-4 2-4 1-3	} Vertex only	120°	Cu-O-V 121°	Li-O-Nb 117°	to 180°
			Cu-O-V 127°	Li-O-Li 122°	
			Cu-O-V 136°	Nb-O-Nb 141°	

this ion has to belong to these numbers of 8-coordination polyhedra. There is no difficulty in building an AX_4 structure from antiprismatic or dodecahedral coordination groups since each X atom has to be common to only two such groups, and this can be done in a variety of ways:

Structure	Type of 8-coordination of M	Elements of coordination polyhedron shared
ZrF ₄	Antiprismatic	8 vertices
ThCl ₄	Dodecahedral	4 edges
ThI ₄	Antiprismatic	2 faces + 1 edge

However, it is presumably impossible to build AX_2 or AX structures from these coordination groups, though it is doubtful if this point has been systematically studied.

The maximum number of regular octahedra that can share a common vertex (subject to the restriction that $x \geq 1$) is six, and there are two arrangements corresponding to those of octahedral interstices around an atom in hexagonal or cubic closest packing. There is at the same time room for eight regular tetrahedra, corresponding to the eight tetrahedral interstices surrounding a close-packed atom. In cubic closest packing these tetrahedral holes are separated by the octahedral ones, but in hexagonal closest packing six of them come together in (face-sharing) pairs, suggesting the possibility that three more (suitably distorted) octahedra could also be fitted in around the common vertex, making a total of nine. We are not aware of a structure in which nine octahedra meet at a point; the highest number observed appears to be eight. This occurs in the Th₃P₄ structure, where there is a bisdisphenoidal arrangement of eight PTh₆ octahedral groups meeting at each Th atom. There is necessarily much edge- and face-sharing between octahedral coordination groups in such a structure of 8:6 coordination.

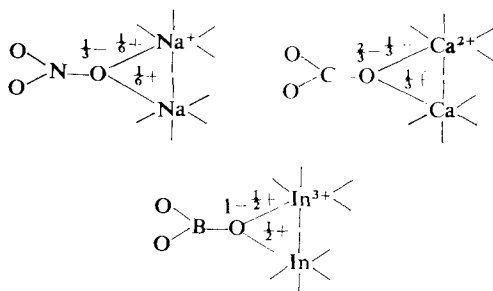
The limitations on the numbers of polyhedra of various kinds that can meet at a point have a direct bearing on the structures and stabilities of certain oxy-salts and complex oxides. Several groups of compounds are of interest in this connection. Systematic studies of cation-rich oxides $M_nM'O_6$ (M = alkali metal) have already produced interesting results. The value of n rises to 8 (for $M(IV)$). As regards accommodating the cations in (approximately regular) tetrahedral and/or octahedral interstices it is advantageous to

have close-packed O atoms, when there are 12 tetrahedral and six octahedral positions per formulaweight. One of the latter is occupied by M' and there is therefore no structural problem for values of $n \leq 5$; in fact, Li₅ReO₆ has a structure rather similar to that of α -NaFeO₂, all cations occupying octahedral interstices. Lithium compounds of this family $M_nM'O_6$ present no difficulty because Li⁺ can go into tetrahedral holes, and this apparently happens in all the following structures (14):

	Tetrahedral	Octahedral
Li ₆ TeO ₆	6 Li	Te
Li ₇ SbO ₆	6 Li	Li, Sb
Li ₈ SnO ₆	6 Li	Li ₂ , Sn

A number of sodium compounds are known, but they are few in number compared with the lithium compounds; for example, 11 compounds Li₈MO₆ are known, two sodium compounds, but none containing K, Rb, or Cs. For the larger alkali metal ions there are insufficient octahedral holes if $n > 5$.

The structures of many groups of anhydrous oxy-salts present geometrical problems which arise from the difficulty of achieving a reasonable charge balance at the oxygen atoms. The negative charge on the O atom of an oxy-ion is balanced by the neighboring cations, as in the series NaNO₃, CaCO₃, and InBO₃:

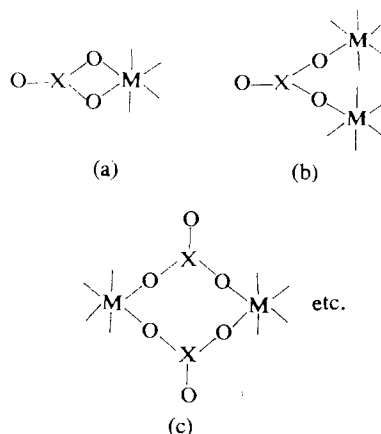


These salts obviously present no problem, but if the charge on O of the oxy-ion is high (for example, -1 in BO_3^{3-} , SiO_4^{4-} , or TeO_6^{6-}) and that on the cation is low, the O atom has to belong simultaneously not only to its own oxy-ion but also to a considerable number of MO_n coordination groups. In Na₄SiO₄, for example, O would have to belong to six (octahedral ?) NaO₆ groups and its own SiO₄ tetrahedron, that is, six octahedra and one tetrahedron meet at a point. It is unlikely that octahedrally coordinated ions such as Na⁺ can present any difficulty, but

as the coordination number of M increases (and the electrostatic strength of the $M-O$ bond decreases) not only does the coordination polyhedron MO_n become larger but also a larger number of these polyhedra have to meet at a point (O atom). The problem is most acute when: the charge on the anion is large; the charge on the cation is small; and the coordination number of the cation is large. These considerations would be expected to be important factors affecting the stabilities of salts such as orthoborates and orthosilicates of large M^+ ions.

An entirely different problem arises if we reduce the charge on O of the oxy-ion, for example, by changing from $CaCO_3$ to $Ca(NO_3)_2$, and/or increase that on M , as in the series: $M(NO_3)_2$, $M(NO_3)_3$, and $M(NO_3)_4$. Consider, for example, the case of $Ti(NO_3)_4$ containing a small ion Ti^{4+} which is normally coordinated octahedrally by 6 O atoms. The $Ti-O$ bond strength would be $2/3$, twice the charge on O of NO_3^- , so that it is impossible to achieve a charge balance. In order to reduce the electrostatic bond strength of the $Ti-O$ bond to $1/3$ the coordination number of Ti^{4+} would have to be increased to the impossibly high value, 12. Clearly this difficulty is most pronounced when: the charge on the anion is small; the charge on the cation is large; and the coordination number of the cation is small. This has a direct bearing on matters such as the crystallization of anhydrous nitrates from aqueous solution and the structures of those anhydrous salts which can be prepared. The charge-balance (or geometrical) difficulty can be avoided by forming a hydrate, when the structural problem becomes entirely different and is different in different hydrates, depending on the degree of hydration of the cation. For example, if the cations are entirely surrounded by water molecules there are no bonds between cations and O atoms of oxy-ions, and it is now a question of packing large $[M(H_2O)_x]^{n+}$ groups and anions, as in hydrates such as $NiSO_4 \cdot 6H_2O$ or $Nd(BrO_3)_3 \cdot 9H_2O$. There is, however, an alternative structure for the anhydrous compound $M(NO_3)_3$, $M(NO_3)_4$, or the corresponding perchlorates, etc., which calls for the rearrangement of the charges on the XO_3^- or XO_4^- ion, from

Only two of the O atoms of a XO_3^- ion are then coordinated to cations, and the ion can function either as a bidentate ligand, (a), or as a bridging ligand, (b) and (c):

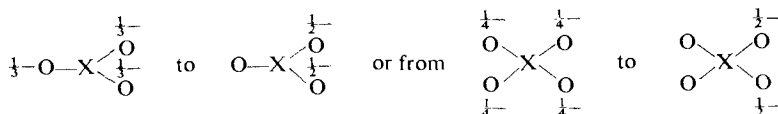


The existence of bidentate NO_3^- groups has been established in a number of anhydrous nitrates [e.g., gaseous $Cu(NO_3)_2$, crystalline $Ti(NO_3)_4$] and nitrate ions [e.g., $Th(NO_3)_6^{2-}$, $Ce(NO_3)_6^{2-}$ and $Ce(NO_3)_6^{3-}$], and this ion acts as a bridging ligand in various crystalline nitrates. This behavior as a bidentate or bridging ligand is not expected to be peculiar to NO_3^- ; it is to be expected for ClO_3^- , BrO_3^- , IO_3^- , ClO_4^- , IO_4^- , and also SO_4^{2-} . In fact the iodate ion behaves in two of the ways shown above, namely, (b), and (c), in anhydrous $Ce(IO_3)_4$ and $Ce(IO_3)_4 \cdot H_2O$, and in $Zr(IO_3)_4$, respectively. The structures of the various anhydrous forms of $Zr(SO_4)_2$ and of its hydrates provide comparable examples of the behavior of the SO_4^{2-} ion.

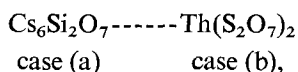
We see that problems of charge balance lead to geometrical difficulties in two distinct classes of salt:

	Charge on O of anion	Cation size	Cation charge
(a)	High	large	low
(b)	Low	small	high

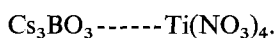
We have discussed (a) as it applies to the extreme cases such as Cs_3BO_3 , Cs_4SiO_4 , or Cs_6TeO_6 , but the problem exists, though in a less acute form, in pyro salts such as $M_6Si_2O_7$ and $M_4P_2O_7$. As in



the case of K_3PO_4 and KH_2PO_4 it can be overcome by the formation of salts such as $K_2H_2P_2O_7$. At the other extreme, case (b), the difficulties arise not only with ions XO_3^- and XO_4^- , as already discussed, but also with ions such as $S_2O_7^{2-}$ if they are combined with cations carrying high charges. Thus the normal ionic disulphate and dichromate of Ti^{4+} or even the salts of the larger Th^{4+} ion would not be possible if the anionic charge is distributed over all (or even six) of the O atoms. For a family of pyro ions we encounter difficulties at both ends of the series:



just as we do for the simpler XO_3^{n-} ions,



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