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# Chemical Symbolism and the Solid State

## A proposal

There are essentially four alternative, but complementary, approaches to describing the solid state. Of these, the three most commonly used are

- 1) Unit cells, formal space group symmetry, etc.
- 2) Archetype lattices such as the rock salt, antiferite, or wurtzite structures.
- 3) The close-packed spheres model.

The problem with the treatments of the solid state found in most introductory freshman texts (and, for that matter, many undergraduate-graduate level inorganic texts) is that a dabbled of all three of these approaches is given without any *single one being used consistently or in sufficient detail to give the student a feel for the subject*. In addition, all three of the above approaches tend to stress the purely formal structural features of the solid state, in contrast to the emphasis which the texts place on bonding interactions between individual atoms when describing the structures of discrete molecules in the liquid and gas phases.

The fundamental nature of the space group description of the solid state cannot, of course, be denied. However, for purposes of an elementary, qualitative introduction to solids the fourth approach, commonly called the coordinated polyhedra approach, offers many descriptive advantages (1). In particular, it tends to place emphasis on bonding interactions and thus represents a natural extension to the solid state of the principles the student has already learned in dealing with discrete molecules. Indeed, the origin of the coordinated polyhedra approach may be found in the extensions which Pfeiffer and Niggli made between 1915 and 1916 of Werner's coordination theory for bridged complexes to the infinitely bridged structures characteristic of crystals (2). The main proponent of the approach today is A. F. Wells, who has developed and refined it through all four editions of his classic text "Structural Inorganic Chemistry" (3) and in several additional books and articles (4).

The coordinated polyhedra approach views a solid as a collection of coordination complexes. The "unit coordination complex" may be as simple as a single atom or it may be a polyatomic polyhedron and the resulting units may either remain discrete in the crystal or may bond together by means of bridging ligands which *infinitely extend the resulting "supercomplex"* in one or more dimensions. The resulting repeat unit or polyhedron generally has the same formula (when one fractionally divides atoms shared between adjacent polyhedra) as that conventionally assigned to the solid and may, therefore, be called the formula repeat unit or simply the chemical repeat unit of the solid. The chemical repeat unit of a crystal is *generally not the same as its formal crystallographic repeat unit*, as can be seen from the figure.

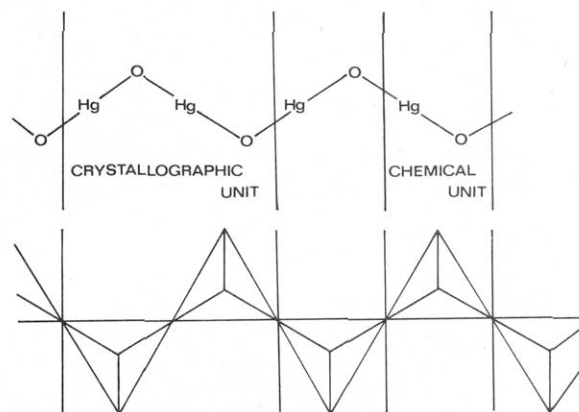
The coordinated polyhedra approach immediately leads to a crude but simple qualitative classification of solid structures into four large categories

- 1) Infinite three dimensional complexes or network structures
- 2) Infinite two dimensional complexes, sheet, or layer structures.
- 3) Infinite one dimensional complexes or chain structures.
- 4) Finite "zero" dimensional complexes or discrete molecular structures

The dimensionality indicates the number of dimensions in which the structural polyhedra or units are infinitely linked, the remaining dimensions interacting only by means of weak intermolecular forces. However, it need not necessarily make a distinction between the types of intramolecular bonding which cause the linking. Thus, NaCl, diamond, and metallic Li may all be classified as solids containing infinite three dimensional complexes though one is linked *via* ionic bonds, one *via* covalent bonds, and one *via* metallic bonds.

The classification is, of course, only approximate as "intra" and "inter" molecular forces gradually shade into one another and the concept of dimensionality becomes correspondingly nebulous. In many cases an interaction which in one structure is classified as intermolecular will in another structure be classified as intramolecular. The best criterion appears to be the relative degree of bonding anisotropy found in a given structure. For example, in  $\text{Al}(\text{OH})_{3(s)}$  the hydrogen bonds between the  $\text{Al}(\text{OH})_3$  layers are much weaker than the oxygen bridges within each layer. They are, therefore, classified as intermolecular and the resulting structure as a two dimensional layer structure. In the pleated sheet structure for silk, on the other hand, the hydrogen bonds holding the protein chains together within each sheet are stronger than the weak van der Waals attractions between the chains in different sheets. They may, therefore, be classified in this case as intramolecular and the resulting structure as a two dimensional layer structure or, more accurately, as a transition type between idealized *one dimensional chain structures and two dimensional layer structures*.

If these qualitative limitations are acceptable, then the above classification suggests a very simple method for extending our current chemical symbolism so as to include the cruder structural facts of solid state chemistry. Currently, in inorganic chemistry at least, no distinction is made between the formula of a discrete molecule such as  $\text{CO}_2$  and the formula of the chemical repeat unit of a solid species of higher dimensionality such as NaCl, although in polymer circles it is common to make the distinction by enclosing the formula of the chemical or structural repeat unit with brackets followed by an  $x$  or  $n$  subscript—for example,  $[\text{SN}]_x$  for the sulfur ni-



The distinction between the crystallographic and chemical repeat units for HgO and for a  $\text{MX}_3$  chain formed by the sharing of two of the vertices of  $\text{MX}_4$  tetrahedrons (from Wells).

Table 1. Examples of the Proposed Symbolism

white phosphorus	P <sub>4</sub>
red or black phosphorus	[P] <sub>2D</sub>
α or β selenium	Se <sub>8</sub>
"metallic" selenium	[Se] <sub>1D</sub>
niobium pentachloride	Nb <sub>2</sub> Cl <sub>10</sub>
niobium tetrachloride	[NbCl <sub>4</sub> ] <sub>1D</sub>
mercury(II) oxide	[HgO] <sub>1D</sub>
zirconium trichloride	[ZrCl <sub>3</sub> ] <sub>1D</sub>
mercury(II) iodide	[HgI <sub>2</sub> ] <sub>2D</sub>
tantalum sulfide	[TaS <sub>2</sub> ] <sub>2D</sub>
potassium chloride	[KCl] <sub>3D</sub>
titanium metal	[Ti] <sub>3D</sub>
potassium tetrachloromercurate(II) hydrate	(K <sup>+</sup> ) <sub>2</sub> [HgCl <sub>4</sub> <sup>2-</sup> ] <sub>1D</sub> (H <sub>2</sub> O)
potassium tetrafluoronickelate(II)	(K <sup>+</sup> ) <sub>2</sub> [NiF <sub>4</sub> <sup>2-</sup> ] <sub>2D</sub>
borax	[Na <sub>2</sub> (H <sub>2</sub> O) <sub>8</sub> <sup>2+</sup> ] <sub>1D</sub> [B <sub>4</sub> O <sub>5</sub> (OH) <sub>4</sub> <sup>2-</sup> ] <sub>1D</sub>
chlorite clay	[Mg <sub>2</sub> Al(OH) <sub>6</sub> <sup>+</sup> ] <sub>2D</sub> [Mg <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub> <sup>-</sup> ] <sub>2D</sub>

Table 2. Some Simplified Formulae for a Variety of Possible Ionic Solids

General Formula	Possible Representation of a Solid Containing:
A[B] <sub>1D</sub>	Discrete cation—Infinite chain anion
A[B] <sub>2D</sub>	Discrete cation—Infinite layer anion
[A] <sub>1D</sub> B	Discrete anion—Infinite chain cation
[A] <sub>2D</sub> B	Discrete anion—Infinite layer cation
[A] <sub>1D</sub> [B] <sub>1D</sub>	Infinite chain cation—Infinite chain anion
[A] <sub>2D</sub> [B] <sub>2D</sub>	Infinite layer cation—Infinite layer anion

In the case of the infinite ion, A or B generally stands for a species which is at least binary in composition. When these formulas are used to represent ionic solids it is best to explicitly indicate charges, as done in Table 1, in order to differentiate them from cases representing the intercalation of neutral species into neutral layer or chain structures.

tride polymer or  $\{-C_2H_4\}_n$  for polyethylene. A reading of Wells' text strongly suggests that a useful elaboration of this practice would be to enclose the formula of the chemical repeat unit of those solids which do not contain discrete molecules with brackets followed by the subscripts 3D, 2D, or 1D to indicate the approximate dimensionality. A 0D or molecular crystal may be represented by its conventional formula as in this case the formula actually represents the composition of a discrete species. Thus, for example, NaCl<sub>(s)</sub> would be written as [NaCl]<sub>3D</sub>, metallic Li as [Li]<sub>3D</sub>, diamond as [C]<sub>3D</sub>, graphite as [C]<sub>2D</sub>, and polymerized sulfur nitride as [SN]<sub>1D</sub>. In some cases it might be advantageous to discriminate between different types of intramolecular bonding. For example, Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> is bonded in three dimensions. However, the bonding between Si and O is essentially polar covalent in nature whereas that between Na and O approaches the idealized ionic extreme. Thus, rather than simply writing [Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>]<sub>3D</sub>, the formula (Na<sup>+</sup>)<sub>2</sub>[Si<sub>2</sub>O<sub>5</sub><sup>2-</sup>]<sub>2D</sub> gives a better description, implying a structure of infinite layer type [Si<sub>2</sub>O<sub>5</sub><sup>2-</sup>]<sub>2D</sub> anions held together by Na<sup>+</sup> ions—two Na<sup>+</sup> ions for every Si<sub>2</sub>O<sub>5</sub><sup>2-</sup> repeat unit in the layer. Additional examples are given in Tables 1 and 2. If one objects to the use of the term dimensionality in the above context (as even discrete molecules have three dimensions) an alternative symbolism such as 3∞, 2∞, and 1∞ could be used instead.

The coordinated polyhedra approach has been used in this discussion to develop the proposed symbolism as the approach seems to naturally suggest the dimensionality classification upon which the symbolism is based. Obviously the same classification and symbolism may be deduced from the other alternative descriptions of the solid state—particularly from the close-packed spheres model in either its conventional or extended form (5).

Just as the formula H<sub>2</sub>O indicates the composition of a discrete molecule but tells us nothing about how the hydrogen and oxygen are linked in the molecule, so the formula [NaCl]<sub>3D</sub> tells us the composition of a solid containing an infinite three dimensional complex but nothing about how the Na and Cl are linked in order to produce this dimensionality. For discrete molecules we have simple procedures, such as the octet rule, EAN rule, electroneutrality principle, etc., which allow the

Table 3. Example Formulas

<i>Chain Structures</i>	
mercury(II) oxide or metallic selenium	[HgO <sub>2</sub> ] <sub>1D</sub> or [Se <sub>2</sub> ] <sub>1D</sub>
selenium dioxide	[SeO <sub>2+1</sub> ] <sub>1D</sub>
gold(III) fluoride	[AuF <sub>2+2</sub> ] <sub>1D</sub>
uranium pentafluoride	[UF <sub>2+4</sub> ] <sub>1D</sub>
copper(II) chloride	[CuCl <sub>4</sub> ] <sub>1D</sub>
niobium(IV) iodide	[NbI <sub>4+2</sub> ] <sub>1D</sub>
zirconium(III) chloride	[ZrCl <sub>3</sub> ] <sub>1D</sub>
U(ac) <sub>4</sub>	[U(ac) <sub>3</sub> ] <sub>2D</sub>
<i>Layer Structures</i>	
boron nitride or graphite	[BN <sub>3</sub> ] <sub>2D</sub> or [C <sub>3</sub> ] <sub>2D</sub>
chromium(III) chloride	[CrCl <sub>3</sub> ] <sub>2D</sub>
cadmium chloride	[CdCl <sub>2</sub> ] <sub>2D</sub>
mercury(II) iodide	[HgI <sub>4</sub> ] <sub>2D</sub>
molybdenite	[MoS <sub>3+3</sub> ] <sub>2D</sub>
<i>Lattice Structures</i>	
rock salt	[NaCl <sub>6</sub> ] <sub>3D</sub>
nickel arsenide	[NiAs <sub>6</sub> ] <sub>3D</sub>
zinc blend or diamond	[ZnS <sub>4</sub> ] <sub>3D</sub> or [C <sub>4</sub> ] <sub>3D</sub>
cesium iodide or bcc metals	[CsI <sub>8</sub> ] <sub>3D</sub> or [A <sub>8</sub> ] <sub>3D</sub>
ccp metals	[A <sub>12</sub> ] <sub>3D</sub> , example [Cu <sub>12</sub> ] <sub>3D</sub>
hcp metals	[A <sub>6+6</sub> ] <sub>3D</sub> , example [Mg <sub>6+6</sub> ] <sub>3D</sub>
fluorite	[CaF <sub>8</sub> ] <sub>3D</sub>
antifluorite	[AB <sub>4</sub> ] <sub>3D</sub> , example [NaO <sub>4</sub> ] <sub>3D</sub>
rutile	[TiO <sub>6</sub> ] <sub>3D</sub>
renew trioxide	[ReO <sub>6</sub> ] <sub>3D</sub>
corundum	[AlO <sub>6</sub> ] <sub>3D</sub>
crystalite or quartz	[SiO <sub>4</sub> ] <sub>3D</sub>
tridymite	[SiO <sub>3+1</sub> ] <sub>3D</sub>

student to deduce probable bonding topologies given the molecular composition of the species. In nonmolecular solids, on the other hand, the number of possible bonding topologies consistent with a given stoichiometry and dimensionality is much larger and often at variance with the simple valence rules used for discrete molecules, as the reader can easily verify by glancing at Wells' text.

If information about the bonding topology is desired, the suggested symbolism may be conveniently combined with the coordination formulas proposed by Hückel for infinite complexes (6). Hückel's procedure is best illustrated by taking a simple example. In NaCl<sub>(s)</sub> each Na is surrounded by six equivalent Cl atoms, giving the formula NaCl<sub>6</sub>. However, each Cl is, in turn, surrounded by five Na atoms in addition to one in the center of the original coordination polyhedron, leaving, in effect, only 1/6 of each Cl atom available to each Na atom. Thus the formula should be written as NaCl<sub>6</sub><sub>6</sub>. This pattern is infinitely repeated in three dimensions, giving the final formula [NaCl<sub>6</sub>]<sub>3D</sub> or the general formula [AB<sub>6</sub>]<sub>3D</sub> for all binary solids having this structure.

In theory it is irrelevant whether one expands the formula around A or B, but, in practice, one usually chooses the least electronegative component as the "central atom". If we are dealing with the structure of an element, for which A = B, one may eliminate the repetition of A in the formula. Thus metals having a body centered cubic structure, derived from the cesium iodide structure [AB<sub>8</sub>]<sub>3D</sub>, are given the general formula [A<sub>8</sub>]<sub>3D</sub> rather than [AA<sub>8</sub>]<sub>3D</sub>.

If the ligands in the coordination polyhedron, which serves as the chemical repeat unit, are nonequivalent, this may be indicated in the formula. Thus αNbI<sub>4</sub> forms infinite chains in which each Nb is surrounded by an octahedron of I atoms, each octahedron sharing two trans edges with the adjacent octahedra in the chain. The resulting formula [NbI<sub>4</sub>]<sub>1D</sub> in-

dicates the nonequivalence of the bridging and terminal I atoms.

Nonequivalence of the ligand atoms may be due to symmetry as well as differences in coordination number; that is, the coordination polyhedron may not be centrosymmetric. Hence the structure for the cubic close-packed metals is  $[A_{\frac{12}{12}}]_{3D}$ , whereas that for hexagonal close-packed metals is  $[A_{\frac{6+6}{6+6}}]_{3D}$ .

Nonstoichiometric phases can also be represented. In the case of cation-or-anion deficient lattices one simply reduces the denominator or numerator of the coordination number ratio to some smaller, nonintegral, average coordination number. Thus  $Fe_{.917}O$  becomes  $[FeO_{\frac{6}{5.502}}]_{3D}$ . When the deviation is due to the incorporation of an excess component in an interstitial site this is indicated by representing the excess as nonequivalent. Thus the interstitial O in  $UO_{2.245}$  becomes  $[UO_{\frac{8+.980}{4}}]_{3D}$  and the excess Zn in  $Zn_{1+7 \times 10^{-5}}O$  becomes  $[ZnO_{\frac{4}{4+2.8 \times 10^{-4}}}]_{3D}$ .

More complex structures can often be obtained by substituting complex groups ( $CO_3^{2-}$ ,  $C_2^{2-}$ ,  $NH_4^+$ , etc.) for A and B in the binary structures. Further examples are given in Table 3, and these illustrate one of the drawbacks of the coordinated polyhedra approach as used in the present context: namely that by removing the infinite complexes from the close-packed reference frame one loses information about the stacking of the chains and sheets found in 1D and 2D solids. Thus both  $PbI_2$  and  $CdCl_2$  are represented by the general formula  $[AB_2]_{2D}$  which gives the correct topology within the layers in each case but fails to show that the sheets are stacked in  $PbI_2$  so that the I atoms are hexagonal close-packed and in  $CdCl_2$  so that the Cl atoms are cubic close-packed.

It has recently come to my attention that virtually the same proposals were made almost forty years ago by Machatschki

(7). He indicated the dimensionality of the complex by prefixing the symbols  $\frac{3}{3}$ ,  $\frac{2}{2}$ , or  $\frac{1}{1}$  to the formula of the repeat unit. The coordination number of each atom or group was indicated by a superscript number of brackets. Finally, a symbol indicating the crystal system was suffixed to the formula ( $c$  = cubic,  $t$  = tetragonal, etc.). Thus NaCl became  $\frac{3}{3}Na^{[6]}Cl^{[6]}c$  and rutile,  $\frac{3}{3}Ti^{[6]}O_2^{[3]}t$ . If one appends a symbol for the crystal system to the formulas in Table 3 they become equivalent to those of Machatschki, with the possible advantage that they avoid the use of a separate number system for both coordination and stoichiometry and employ, in keeping with current chemical symbolism, only subscripts.

As pointed out above, the coordinated polyhedra approach, by treating solids as infinitely bridged coordination complexes, makes use of the same principles the student has learned in dealing with the structures of discrete molecules and hence is useful in teaching the simpler aspects of solid state structure at the introductory level.

#### Literature Cited

- (1) For an example of a recent elementary text using the coordinated polyhedra approach see Jolly, W. L., "The Principles of Inorganic Chemistry," McGraw-Hill, New York, 1976, Chap. 10.
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- (5) Ho, S., and Douglas, B., J. CHEM. EDUC., 45, 474 (1968); 46, 207 (1969); 49, 74 (1972).
- (6) Hückel, W., "Structural Chemistry of Inorganic Compounds," Elsevier, New York, 1951, Vol. II, Chap. VII. Hückel indicates the dimensionality by appending a descriptive phrase rather than a symbol to his formulae.
- (7) Machatschki, F., *Naturwissenschaften*, 27, 670, 685 (1939).