Stoichiometry, Coordination, and Interatomic Distances in Simple Valence Crystals

STAFFAN HANSEN

Inorganic Chemistry 2, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

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A simple valence or haplotype crystal is defined as a valence crystal of binary composition A_xB_y , with one coordination number, CN(A), for all cations and one, CN(B), for all anions. Valence crystals have electroneutral formulas with respect to formal atomic valences (V_A, V_B) and each cation is surrounded entirely by anions and vice versa. Known haplotype structures include a majority of textbook examples of binary inorganic structures. Two simple rules apply to haplotypes: $x \cdot V_A = y \cdot V_B$ and $x \cdot \text{CN}(A) = y \cdot \text{CN}(B)$. These two rules strongly limit the number of possible combinations of atomic valence, composition, and coordination. A clear connection is shown to exist in known haplotypes between the coordination number of the majority atom and the dimensionality of strong bonding, which in turn has a great influence on crystal properties. In haplotypes with three-dimensional bonding, an observed relationship between composition and interatomic distances is shown to be a consequence of the rather regular coordination figures present in this group of structures. © 1993 Academic Press, Inc.

Introduction

Textbooks in general and inorganic chemistry, solid state physics, materials science, and mineralogy invariably feature a section on the crystal structure of binary inorganic compounds, A_xB_y , which includes structure types such as NaCl, CsCl, ZnS (spharlerite and wurtzite), CaF₂, TiO₂ (rutile), Cdl₂, and SiO₂ (cristobalite and tridymite). Problems involving the calculation of interatomic distances in these structure types, using the Pythagorean theorem, are usually found among the excercises accompanying this section in the texts.

In this context it is natural to make two observations. First, a relationship exists between coordination numbers of atoms and coefficients in the formula. For each of the two kinds of atom, the product of coordination number and coefficient is the same; e.g., for rutile, $^{vi}Ti^{iii}O_2$, the products are $6 \times 1 = 3 \times 2$ (superscripts in formulae denote coordination numbers). Second, in the AB

compounds listed above, the anion-anion and cation-cation distances are equal, while in the AB_2 compounds the anion-anion distances are shorter than the cation-cation distances. The first of these observations was made long ago by V. M. Goldschmidt, see review in Ref. (1), but this relationship between coordination number and composition is only rarely discussed in textbooks. For an exception see Ref. (2), pp. 264-265. The second observation concerning interatomic distances and composition is not made in textbooks, as far as I have seen.

On the other hand, it is always mentioned that compounds have stoichiometries which are related to the formal atomic valences by the requirement of electroneutrality; e.g., for TiO_2 with Ti(4+) and O(2-) the numbers of positive and negative charges are the same since $1 \times 4 = 2 \times 2$.

The materials mentioned above belong to what is sometimes loosely referred to as ionic compounds and they are also valence crystals according to the definition of El-

lison and Navrotsky (3), which states that "Valence crystals have bulk stoichiometries that are electroneutral with respect to formal atomic valence, and structures in which cation sites are formed entirely by anions and vice versa." The authors then go on to study the restrictions this definition puts on the possible combinations of stoichiometry, coordination number, and atomic valences in rather general cases, and they also include bond strengths in their treatment.

In this paper I examine the simplest valence crystals and their properties from a purely geometrical point of view, without making assumptions concerning bond strengths, ionic radii, atomic contacts, etc.

Simple Valence Crystals

Consider a binary valence crystal $A_{\lambda}B_{y}$, in which the cation valences $V_{A}=1,2,\ldots$, 6 and anion valences $V_{B}=1,2,3$ are allowed. The law of electroneutrality can be formulated as

$$x \cdot V_A = y \cdot V_B \tag{1}$$

and with valences as defined above a total of 13 stoichiometries can be generated, which are listed in the left column of Table I. Please note that the definition of valences given above automatically excludes all mixed-valence compounds.

From the fact that cations are surrounded by anions and vice versa a stoichiometrycoordination rule has been derived by O'Keeffe and Hyde (4, 5), which states that in the binary case

$$x \cdot \langle \text{CN}(A) \rangle = y \cdot \langle \text{CN}(B) \rangle,$$
 (2)

where $\langle \text{CN}(A) \rangle$ is the average coordination number of the cations and $\langle \text{CN}(B) \rangle$ that of the anions. As an illustration take the PbCl₂ structure, which can be described as ^{ix}Pb^vCl^{iv}Cl, i.e., the average coordination number of Cl is 4.5 and Eq. (2) thus gives $1 \times 9 = 2 \times 4.5$.

I now define a simple valence crystal as

a valence crystal with a structure obeying Eq. (2) in the stricter form

$$x \cdot CN(A) = y \cdot CN(B),$$
 (3)

where CN(A) and CN(B) are the coordination numbers (the number of nearest neighbors) of A and B. This means that the cations all have one specific coordination number and so do the anions. A selection of well-known structure types that obey Eqs (1) and (3) is presented in Table I.

In order to keep the presentation as brief as possible, the atomic valences $V_A = 7$, 8 and $V_B = 4$ were not included among those allowed, because they generate many stoichiometries without known examples. Only a few simple valence structures, e.g., OsO₄, are excluded from Table I by this procedure.

A majority of the structure types found in textbooks, even some advanced ones, are represented in Table I; i.e., they are simple valence structures. It is also worth noting that several of the AB_n and A_nB structures in Table I represent examples of the same geometric arrangement of points in space; i.e., they exhibit a structure and antistructure relationship.

I have been able to find examples of simple valence structures illustrating the possible stoichiometries in 11 of the 13 cases, the exceptions being the compositions A_3B_5 and A_2B_5 . The formula $^{\mathsf{v}}A_2{}^{\mathsf{ii}}B_5$ fits an oxide of a pentavalent metal, but no such simple structure is known to me. On the contrary, it is well known that A_2O_5 compounds have complicated structures with oxygen atoms (and sometimes A atoms as well) exhibiting more than one coordination number in a specific structure; cf. the many forms of Nb₂O₅.

Stoichiometry and Coordination

Equation (3) is now used to investigate the possible compositions of simple valence crystals with a specific cation or anion coordination number, when coordination numbers less than or equal to 9 are taken into consideration; see Tables II and III for results. By inspection, it can be concluded

TABLE 1
Some Simple Valence Structures

Composition	Examples		
$A_{3}B$	ⁱ H ₃ ⁱⁱⁱ N (ammonia), ^a ⁱⁱ Cu ₃ ^{vi} N (anti-ReO ₃)		
A_2B	$^{i}H_{2}^{ii}O,^{a}$ $^{ii}Cu_{2}^{iv}O,^{iii}Cs_{2}^{vi}O$ (anti-CdCl ₂), $^{iii}Tl_{2}^{vi}S$ (anti-CdL ₂), $^{iv}Na_{2}^{viii}O$ (anti-CaF ₂)		
A_3B_2	^{iv} Mg ₃ ^{vi} N ₂ (anti-bixbyite)		
AB	ⁱ C ⁱ O, ^a ⁱⁱ Hg ⁱⁱ O (orthorhombic), ⁱⁱ Hg ⁱⁱ S (cinnabar), ⁱⁱ Au ⁱⁱ J, ⁱⁱⁱ B ⁱⁱⁱ N, ^{iv} Zn ^{iv} S (spharlerite), ^{iv} Zn ^{iv} O (wurtzite-type), ^{iv} Be ^{iv} O (β), ^{iv} Pb ^{iv} O (red), ^{iv} Pt ^{iv} S (cooperite), ^v Ni ^v S (millerite), ^{vi} Na ^{vi} Cl, ^{vi} Ni ^v As, ^{viii} Cs ^{viii} Cl		
A_3B_4	$^{\text{iv}}\text{Si}_3^{\text{iii}}\text{N}_4, ^{\text{viii}}\text{Th}_3^{\text{vi}}P_4$		
A_2B_3	$^{\text{iii}}P_4^{\text{ii}}O_6$, $^{\text{iii}}As_2^{\text{ii}}O_3$ (monoclinic), $^{\text{iii}}B_2^{\text{ii}}O_3$ (I), $^{\text{vi}}Al_2^{\text{iv}}O_3$ (corundum), $^{\text{vi}}(Mn,Fe)_2^{\text{iv}}O_3$ (bixbyite)		
A_3B_5	-		
AB_2	ii C $^{iO}_{2}$, a iv Si $^{iiO}_{2}$, b iv Hg ii I ₂ (red), iv Si ii S ₂ , iv Pd ii Cl ₂ (α and β), vi Ti iii O ₂ (rutile and anatase), vi Pb iii O ₂ (α), vi Cd iiI I ₂ , vi Cd iiC Cl ₂ , vi Mo iiS S ₂ , viiC Ca iv F ₂		
A_2B_5	~		
AB_3	$^{\text{iii}}B^{\text{i}}Cl_3$, a $^{\text{vi}}Ti^{\text{ii}}Cl_3$ (β), $^{\text{vi}}Bi^{\text{ii}}I_3$, $^{\text{vi}}Cr^{\text{ii}}Cl_3$, $^{\text{vi}}Re^{\text{ii}}O_3$, $^{\text{vi}}Re^{\text{ii}}O_3$ (III, anti-Fe ₃ N), $^{\text{vi}}Al^{\text{ii}}F_3$ (β), $^{\text{ix}}U^{\text{iii}}Cl_3$		
AB_4	ivSilF ₄ ," viiiTh"Cl ₄		
AB_5	YSb ⁱ Cl ₅ a		
AB_6	$^{\text{vi}}\text{U}^{\text{i}}\text{C}\text{I}_{6}^{}a}$		

Note. Superscripts denote coordination numbers.

that for a specific coordination number between 6 and 12 of the 13 stoichiometries allowed by electroneutrality cannot exist as simple valence structures. Note that AB stoichiometry is possible in all cases considered in Tables II and III. AB compounds have CN(A) = CN(B) according to Eq. (3); examples of structure types with coordination number 1 to 6 and one with CN = 8

are listed in Table I. In FeSi both Fe and Si are seven-coordinated, but this phase does not obey Eq. (1) and has thus not been included in Table I.

As another example, consider the important group of tetrahedral structures, which contains tetrahedrally coordinated cations, i.e., CN(A) = 4. This group of structures includes important semiconduc-

TABLE II STOICHIOMETRY AS A FUNCTION OF CATION COORDINATION NUMBER $\mathrm{CN}(A)$ IN SIMPLE VALENCE STRUCTURES

STOICHIOMETRY	AS	A	Function	OF	Anion
Coordination	Nимі	BER	CN(B)	IN	SIMPLE
VALENCE STRUCT	URES				

TABLE III

Possible stoichiometries	CN(B)	Possible stoichiometries
A_3B , A_2B , AB	1	$AB, AB_2, AB_3, AB_4, AB_5, AB_6$
$A_3B, A_2B, A_3B_2, AB, AB_2$	2	A_2B , AB , A_2B_3 , AB_2 , A_2B_5 , AB_3 , AB_4
$A_3B, A_2B, AB, A_2B_3, AB_3$	3	A_3B , A_3B_2 , AB , A_3B_4 , A_3B_5 , AB_2 , AB_3
A_2B , A_3B_2 , AB , A_3B_4 , AB_2 , AB_4	4	A_2B, AB, A_2B_3, AB_2
AB, A_3B_5, A_2B_5, AB_5	5	AB
A_3B_2 , AB , A_2B_3 , AB_2 , AB_3 , AB_6	6	A_1B , A_2B , A_3B_2 , AB , A_3B_4 , A_2B_3
AB	7	AB
AB , A_3B_4 , AB_2 , AB_4	8	A_2B , AB
AB , A_2B_3 , AB_3	9	A_3B , A_3B_2 , AB
	A ₃ B, A ₂ B, AB A ₃ B, A ₂ B, A ₃ B ₂ , AB, AB ₂ A ₃ B, A ₂ B, AB, A ₂ B ₃ , AB ₃ A ₂ B, A ₃ B ₂ , AB, A ₃ B ₄ , AB ₂ , AB ₄ AB, A ₃ B ₅ , A ₂ B ₅ , AB ₅ A ₃ B ₂ , AB, A ₂ B ₃ , AB ₂ , AB ₃ , AB ₆ AB AB, A ₃ B ₄ , AB ₂ , AB ₄	A ₃ B, A ₂ B, AB A ₃ B, A ₂ B, A ₃ B ₂ , AB, AB ₂ 2 A ₃ B, A ₂ B, AB, A ₂ B ₃ , AB ₃ 3 A ₂ B, A ₃ B ₂ , AB, A ₃ B ₄ , AB ₂ , AB ₄ 4 AB, A ₃ B ₅ , A ₂ B ₅ , AB ₅ 5 A ₃ B ₂ , AB, A ₂ B ₃ , AB ₂ , AB ₃ , AB ₆ 6 AB 7 AB, A ₃ B ₄ , AB ₂ , AB ₄ 8

^aPlus other molecular structure types with one-coordinated ligands.

^bQuartz, cristobalite, tridymite, keatite, and coesite.

tors (GaAs and CdS), ceramics (Si_3N_4), and geological materials (SiO_2). Only six compositions can be expected in simple tetrahedral structures. The absence of simple tetrahedral structures of composition AB_3 and A_2B_3 is especially striking, as is the fact that the anion coordination number cannot assume the values 5 or 7 in this type of structure.

It is also noteworthy that simple molecular structures, i.e. simple compounds with one-coordinated ligands, cannot exist for five compositions, i.e., A_3B_2 , A_3B_4 , A_2B_3 , A_3B_5 , and A_2B_5 .

Coordination and Dimensionality of Bonding

The number of directions associated with strong bonding has a decisive influence on the physical properties of a crystal. These properties include crystal morphology, mechanical strength, catalytic activity, etc. If the dimensionality of strong bonding in simple crystal structures is examined as a function of coordination number of the majority species, a straightforward relationship is revealed; see Table IV.

If the majority ion is one-coordinated, a typical molecular solid is formed. Typical properties of such solids are low melting point, high vapor pressure, and softness (low mechanical strength). A two-coordinated majority ion apparently puts no constraints on the dimensionality of the crystal, while for three- and four-coordinated majority ions only 2- and 3-dimensional structures are represented in Table IV. For higher coordination numbers, i.e., 5 to 9, only 3-dimensional simple structures are present. Crystals with 1- or 2-dimensional strong bonding exhibit strongly anisotropic properties.

A similar general relationship between coordination number and dimensionality of bonding has been described before (Ref. (6, pp. 57-58)) in structures composed of one element ("systems of p-connected points").

Interatomic Distances in 3D-Structures

By consideration of the geometrical properties of the most regular coordination figures XY_n , i.e., those depicted in Fig. 1, a simple relationship between composition and interatomic distances in simple 3-dimensional structures can be established.

Figure 2 shows that an almost linear relationship exists for the ratio of center-vertex distance, d(X-Y), to vertex-vertex distance, d(Y-Y), versus coordination number for these high-symmetry coordination figures. This relationship is more conveniently written as

$$CN(X) = k \cdot [d(X-Y)/d(Y-Y)] + m, \quad (4)$$

where k is the slope and m the intercept of the line. I note in passing that the distance ratio d(A-B)/d(B-B) is formally related to the radius ratio, which, following Goldschmidt (1), is considered to determine the coordination number and structure type in a majority of textbooks. The two ratios are related by the expression

$$d(A-B)/d(B-B) = \frac{1}{2}[(r_A/r_B) + 1], \quad (5)$$

where r_x is the ionic radius of X.

Since Eq. (4) is applicable to both cationand anion-centered polyhedra the two expressions can be combined as

$$[CN(A) - m]/[CN(B) - m] = d(A-A)/d(B-B).$$
 (6)

As a consequence of the definition of valence crystal it follows that d(A-B) is shorter than d(A-A) or d(B-B), which together with Eqs. (3) and (6) leads to the following composition-distance relationships:

if
$$x = y$$
 then $d(A-B)$
 $< d(A-A) = d(B-B)$ (7)

if
$$x < y$$
 then $d(A-B) < d(B-B)$
 $< d(A-A)$ (8)

if
$$x > y$$
 then $d(A-B) < d(A-A)$
 $< d(B-B)$. (9)

TABLE IV

Dimensionality of Strong Bonding as a Function of Coordination Number of the Majority Species in Simple Structure Types Included in Table I.

CN	0-D (molecules)	1-D (chains)	2-D (layers)	3-D (networks)
1	H ₃ N, H ₂ O, CO, CO ₂ , BCl ₃ , SiF ₄ , SbCl ₅ , UCl ₆		_	
2	P ₄ O ₆ , PdCl ₂	AuI, HgO, HgS, PdCl ₂ , SiS ₂ , TiCl ₃	As ₂ O ₃ , HgI ₂ , BiI ₃ , CrCl ₃	Cu_3N/ReO_3 , ReO_3 (III), AlF_3 , SiO_2 , Cu_2O , B_2O_3 , $ThCl_4$
3	_	_	$Cs_2O/CdCl_2$, Tl_2S/CdI_2 , BN , MoS_2	Si ₃ N ₄ , PbO ₂ , TiO ₂ (2 forms), UCl ₃
4		_	РЬО	Na ₂ O/CaF ₂ , Mg ₃ N ₂ / (Mn, Fe) ₂ O ₃ , ZnS, ZnO, PtS, BeO, Al ₂ O ₃
5			-	NiS
6	_	_	_	NaCl, NiAs, Th ₃ P ₄
7		_	_	_
8	-	_	-	CsCl
9	_	-	-	_

Note. Weak cation-anion interactions, hydrogen bonds, and van der Waals bonds are neglected.

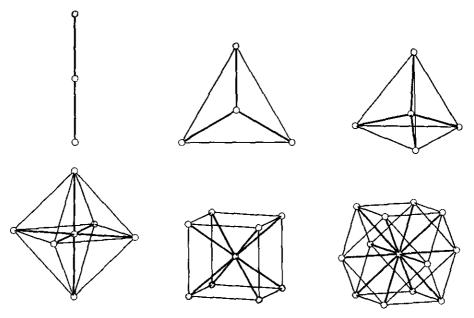


Fig. 1. High-symmetry XY_n coordination figures (n = 2, 3, 4, 6, 8, 12) drawn with constant centervertex distance, d(X-Y).

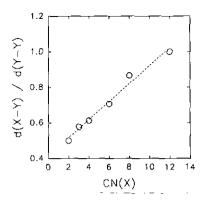


Fig. 2. Center-vertex distance, d(X-Y), divided by vertex-vertex distance, d(Y-Y), versus coordination number, CN(X), for the coordination figures in Fig. 1. Dashed regression line: $d(X-Y)/d(Y-Y) = 0.0506 \cdot \text{CN}(X) + 0.415$ (correlation coefficient = 0.991).

These rules, Eqs. (7–9), are found to be almost true for the three-dimensional structures in Table IV and the actual average values have been calculated, mostly using modern structure refinements found in *Structure Reports*. The results are presented in Table V, where it can be seen that Eqs. (8) and (9) hold for the average values in all of the listed structures with x not equal to y. In the case of AB structures Eq. (7) predicts equal anion—anion and cation—cation distances. Among the eight AB structures this holds exactly for high-temperature BeO, spharlerite ZnS, wurtzite-type ZnO, NaCl, and CsCl.

It almost holds for NiAs, which is a bit surprising since NiAs is a metallic phase with very formal atomic valencies. Equation (7) is only approximately true in the case of cooperite, PtS, but the real structure of cooperite can be idealized (7) and this procedure makes the two distances exactly equal. The real cooperite structure (8) is tetragonal with an axial ratio c/a = 1.761 and the atoms are in special positions with fixed coordinates. If the axial ratio is idealized to c/a = 2, the shortest Pt-Pt and S-S distances become equal.

In the fascinating structure of millerite (9), NiS, the Ni atom is surrounded by five S atoms forming a square pyramid, with an

average Ni–S distance of 2.31 Å. The S atom is surrounded by five Ni atoms also forming a square pyramid with an average S–Ni distance of 2.31 Å. The eight shortest S–S distances in millerite average to 3.28 Å, while the Ni–Ni distances are 3.15 Å $(2\times)$ and 2.53 Å $(2\times)$. Two of the Ni–Ni distances are thus considerably shorter than predicted by Eq. (7) and indicate the presence of metal–metal bonding. It must also be kept in mind that no completely regular XY_5 polyhedron exists, because all ligand atoms (Y atoms) cannot be symmetry equivalent.

The reason that Eqs. (7-9) do not hold for most low-dimensional (0-2 D) structures in Table IV, is the irregular coordination of A or B in many of these materials.

Conclusions

It has recently been stated (10) that "One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition." The present paper had addressed a less fundamental, though associated question, i.e., what we mean by a simple crystal structure and what basic restrictions are applicable to such structures before the question of minimum energy is considered.

In this work I have tried to show that simple valence crystals constitutes a group of important materials exhibiting fundamental crystal chemical relationships that make them unique. For this reason, I propose the terms haplotype crystals and haplotype structures (from Greek haplous simple) as synonyms for the concepts simple valence crystals and simple valence structures, as defined in this paper. It will probably be wise to restrict the haplotype concept to structures with relatively few position and unit cell parameters, in order to exclude, for example, long-period polytypes (ZnS, CdI₂, etc.) and synthetic SiO₂ polymorphs with complex tetrahedral framework structures.

Haplotype structures, by definition, ex-

TABLE V

Average Anion-Anion Distance and Cation-Cation Distance Relative to Average Cation-Anion
Distance for Simple Valence Crystals with Strong Bonding in Three Dimensions

Composition	Structure	$\langle d(BB) \rangle / \langle d(AB) \rangle$	$\langle d(AA)\rangle/\langle d(AB)\rangle$
A_3B	Cu ₃ N	2.00	1.41
A_2B	Cu ₂ O	2.00	1.63
	Na ₂ O	1.63	1.15
A_3B_2	Mg_3N_2	1.65	1.47
AB	BeO	1.65	1.65
	ZnS	1.63	1.63
	ZnO	1.63	1.63
	PtS	1.44	1.50
	NiS	1.42	1.23
	NiAs	1.34	1.37
	NaCl	1.41	1.41
	CsCl	1.15	1.15
A_3B_4	Si ₃ N ₄	1.63	1.73
,	Th₃P₄	1.30	1.35
A_2B_3	B_2O_3	1.73	1.82
	Al_2O_3	1.42	1.54
	$(Mn, Fe)_2O_3$	1.45	1.65
AB_2	SiO ₂ (five forms)	1.63	1.91-1.95
_	PbO_2	1.41	1.74
	TiO ₂ (anatase)	1.45	1.56
	TiO ₂ (rutile)	1.47	1.76
	CaF ₂	1.15	1.63
AB_3	ReO ₃	1.41	2.00
	ReO ₃ (III)	1.41	1.82
	AlF ₃	1.41	1.94
	UCÍ,	1.22	1.56
AB_4	ThCl₄	1.26	1.65

hibit simple relationships between atomic valence, coordination number, and compound stoichiometry and it has been shown that these relationships impose rather severe restrictions on possible combinations of the three. Haplotypes are among the simplest possible binary compounds. It has been shown here that many materials emphasized in university solid state courses in fact belong to the group of haplotypes, and here the coordination-stoichiometry rule of O'Keeffe and Hyde (4, 5) is a useful aid when it comes to analyzing and memorizing structure types. The haplotypes exhibit a clear connection between the coordination of the majority species and the dimensionality of the crystal structure, which in turn has

great influence on the physical properties of the crystal. The relative magnitude of the anion-anion and cation-cation distances in three-dimensional haplotype structures has been shown to be related to crystal stoichiometry. This relationship follows from the fact that both cation- and anion-centered polyhedra in 3-D haplotypes tend to be rather regular.

It is my hope that the recognition of haplotypes as a distinct group among inorganic compounds will stimulate further research in this area of solid state chemistry, in order to resolve the long-term problem of understanding the relationship between chemical composition, structure, and physical properties (1, 11) in simple solids.

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