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The coordination number rule and its implications – a review

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In memoriam Rudolf Hoppe on the occasion of his 100th birthday

We give a review on the coordination number rule and its implications. We demonstrate how even rather complex (non-molecular) structures can be rationalized and sometimes even predicted starting from primary coordination numbers of cations only, and we show how connectivity formulas of a Niggli-type can be inferred from such a simple starting point. Furthermore, we derive a measure to describe the segregation of different ions within the general matrix and we point out that it can be due not only to chemical disparities of the components but also to simple numerical relations between stoichiometric coefficients and coordination numbers. It can be shown that Pauling's electrostatic valence rule must sometimes necessarily be violated depending on such numerical relations. We finally address the principle of electrostatic balance as a driving force for creating certain topologies which seem surprising at first glance, and we may thereby help to "reconcile" with the "violations" of Pauling's rule.

Introduction

"Sizes" of atomic and molecular species, their dependence on the type of interaction with other ones and on their general embedment in a structured collective have ever been important topoi of scientific debate in crystal chemistry. Going along with various definitions of size different views on its effect on structuring the surroundings of an atom or ion have developed which were biased by the "parentage" of the scientists from a particular field of their scientific discipline. Even the description of "surroundings" was ambiguous in many cases, the question "who is neighbour or not" or "who interacts with a central atom and to which degree" has led to many debates in literature of which we may mention only one as a representative.[1] Rudolf Hoppe has contributed to this discussion in a beneficial way by denominating the ambiguities[2] and by giving help to overcome them.[3] The concept of "coordination" has been of greatest importance in his theoretical work but also in the vast output of his synthetical achievements. As another highlight we may remember his efforts to study the interdependency of topology and energy by bringing Madelung – type contributions into closer attention of crystal chemists. And there too coordination numbers and their definition have played a decisive role in some of his "shortcut" approaches to calculate the electrostatic part of lattice energy.[4] He has even used such calculations to point at possible errors in structure determinations, though this has not always helped him to avoid some shortcomings in the crystallographic work on his compounds.

In honour of his achievement in crystal chemistry we would like to take over the baton from him and present a review on some aspects and consequences of coordination numbers. However, other than in his approach, we do not discuss differences in coordination power as explained by a detailed study of cation-anion distances. Our definition of coordination is rather a topological one. Howsoever the coordination is defined, it be by Brunner's largest gap[17] or by Wigner-Seitz-like considerations, we then take each neighbour as given to define the type of a coordination polyhedron, and we then discuss how this polyhedron is embedded in the total crystal structure and catenated with the other ones. A polyhedron with "more or less strong corners" cannot be fancied nor can its catenation with adjacent moieties be envisaged. The following treatment will only make sense in this restricted definition of coordination.

The coordination number rule and its implications

The interpretation of inorganic crystal structures in crystal chemistry is mostly based on rules which have been put up in an analysis of many structure types and on simple assumptions such as size relations of the atoms or ions and on concepts such as the drive for electrostatic balance. Seeming violations of such rules were sometimes found to be puzzling and the search for alternative explanations has filled many a line in publications sometimes ending up wearily with the insight that rules are not laws. We must remind that there is something like a rank in our rules which must be respected, and that *the coordination number rule* has "a higher rank" than some other

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ones. In the following we will try to define its rank in more detail.

It is trivial to note that the number of contacts of the cations to the anions in a solid-state structure is the same as those of the anions to the cations. It was perhaps O'Keeffe and Hyde[5] who first pointed out some consequences of this simple statement in defining the so-called "coordination number rule". In an earlier paper[6] we have examined the outcome of this rule in more detail in order to show that it may be used as a powerful tool to rationalize inorganic coordination structures and that even very complex topologies can easily be explained as the result of specific ratios and relations between coordination numbers and stoichiometric coefficients.

Theoretical background and mathematical description of the coordination number rule

Let $\mathbf{A}_{\mathbf{a}}^{[\mathbf{p}]}\mathbf{B}_{\mathbf{b}}^{[\mathbf{q}]}\mathbf{X}_{\mathbf{c}}^{[\mathbf{r}]}$ be a ternary compound with two different cationic components (A, B) in an anionic matrix (X) where *p, q* and *r* are the respective coordination numbers of the A-, B- and X-type components.

The coordination number rule expresses the simple fact that the number of coordination-contacts (cc) of the anions equals those of the cations.

- Coordination number rule: $ap+bq=cr$
- The contribution of the different cations to the coordination of the anions is given by: $r=r_A+r_B$, where $r_A=ap/c$ and $r_B=bq/c$

The general "*principle of symmetry*" and the "*principle of simplicity*" seemingly play an important role in the formation of crystal structures. They both illustrate the tendency to create like interactions and surroundings for like atomic species and they impose that the topology of the structure will meet the "*simplest solution*" in the numerical relations between coordination numbers and stoichiometric coefficients. (When speaking of such "principles" or "rules" we may not misunderstand this terminology in a way as to reverse cause-effect relationships. "High symmetry" or "simplest solutions" are the result of special bonding interactions in a high dimensional force field. However, in an analysis of crystal structures we often tend to extract some "principles governing the topology".)

The calculation of *r* from the coefficients *p* and *q* may lead to non-integer numbers. However, in this topological context coordination numbers (cc) are defined as integers ($cc\in\mathbb{Z}$), therefore the *principle of simplicity* asking for the *simplest numerical solution* will require that *r*, r_A and r_B must be expressed by a number of integers adjoining these non-integer values given as $\lfloor n\rfloor$ and $\lceil m\rceil$ with $m=n+1$ of which their arithmetic mean gives the respective values.

Therefore, we denominate such integers as

- $\lfloor \mathrm{r}\rfloor=\mathrm{r}_0$ $\lfloor \mathrm{r}_\mathrm{A}\rfloor=r_{A_0}$ $\lfloor \mathrm{r}_\mathrm{B}\rfloor=r_{B_0}$
- $\lceil \mathrm{r}\rceil=\mathrm{r}_1$ $\lceil \mathrm{r}_\mathrm{A}\rceil=r_{A_1}$ $\lceil \mathrm{r}_\mathrm{B}\rceil=r_{B_1}$

(Gauss brackets indicate lower or higher integer values next to the rational non-integer numbers ($\mathbb{Q}$) resulting from the calculation of *r*, r_A and r_B)

The respective number of coordination contacts will then be

- $\mathrm{v}_0\, r_{A_0}+\mathrm{v}_1 r_{A_1}=\mathrm{ap}$ and $\mathrm{w}_0 r_{B_0}+\mathrm{w}_1 r_{B_1}=\mathrm{bq}$

where v_i and w_i are the numbers of adjoining lower or higher integers needed to sum up to the non-integer values of *r*, r_A and r_B. This also yields the following simple linear equations:

- $\mathrm{v}_0+\mathrm{v}_1=\mathrm{c}$ and $\mathrm{w}_0+\mathrm{w}_1=\mathrm{c}$

Under such mathematical conditions we will encounter three different cases:

(1) r_A and $r_B\in\mathbb{Z}$ gives the simple numerical solution $X_c^{[r_A+r_B]}$ (for the last part of the general formula $\mathrm{A}_a{}^{[p]}\mathrm{B}_b{}^{[q]}\mathrm{X}_c{}^{[r]}$). An example for such a case will be the perovskite type $\mathrm{Ba}^{[12]}\,\mathrm{Ti}^{[6]}\,\mathrm{O}_3^{[4+2]}$.

(2) $\mathrm{r_A}\in\mathbb{Z}$, $\mathrm{r_B}\in\mathbb{Z}$ or $\mathrm{r_A}\in\mathbb{Z}$, $\mathrm{r_B}\in\mathbb{Z}$: $X_c^{[r_A+\frac{w_0 r_{B_0}+w_1 r_{B_1}}{c}]}$ or $X_c^{[\frac{v_0 r_{A_0}+v_1 r_{A_1}}{c}+\,r_B]}$

We give $\mathrm{Th}^{[8]}\mathrm{Ti}_2^{[6]}\mathrm{O}_6^{[\frac{8}{6}+2]}$ as an example for the latter case where $r_B=2$, $v_0=4$, $r_{A_0}=1$, $v_1=2$ and $r_{A_1}=2$.

(3) $\mathrm{r_A}$, $\mathrm{r_B}\in\mathbb{Z}$: $X_c^{\left[\frac{v_0 r_{A_0}+v_1 r_{A_1}+w_0 r_{B_0}+w_1 r_{B_1}}{c}\right]}$

This general case may be exemplified by the topology of the K_2NiF_4-type. A first coordinative information is given by $\mathrm{K}_2^{[9]}\mathrm{Ni}^{[6]}\mathrm{F}_4^{[6]}$ leaving open how many K and Ni cations contribute to the coordination of F. The total coordination number of 6 must be split up in a 18:6 relation giving 4.5 and 1.5 as the respective coordination numbers. In this case $r_{A_0}=4$, $r_{A_1}=5$, $v_0=2$, $v_1=2$ and $r_{B_0}=1$, $r_{B_1}=2$, $w_0=2$, $w_1=2$. Filling in these numbers into the general formula will give the superscript [(2×*4*+2×*5*+2×*1*+2×*2*)/4] (where the coordination numbers themselves are given in italics). We have then to group these products in such a way as to have pairs amounting to the value of $r=r_A+r_B=6$, i.e. twice [4+2] and twice [5+1].This means that there must be at least two crystallographically different anions F(1) and F(2) with an integer number of the corresponding cations surrounding them to give a full coordination description as $\mathrm{K}_2^{[9]}\mathrm{Ni}^{[6]}\mathrm{F}(1)_2^{[4+2]}\mathrm{F}(2)_2^{[5+1]}$. (In a very general case this could also require up to four separate Wyckoff sites for the anions in the lattice.)

Outcome and earnings of applying the coordination number rule

This general overview should emphasize that even though we postulate the application of the simplest numerical solutions according to the *principles of symmetry and simplicity* we will find rather complex constellations in many cases even for "seemingly simple sets" of coordination numbers. Certain combinations of cation coordination numbers together with their stoichiometric coefficients will necessarily imply a distribution of the corresponding anions on several independent sites in the unit cell depending on the overall symmetry of the structure as represented in its space-group. Indeed, these simple calculations may already help to understand why some space-group types which seem possible at first hand will not offer the necessary type and number of Wyckoff sites to "host" the respective number of equivalent or non-equivalent groups of anions.

Given the whole set of individual coordination contacts of cations and anions we can even envisage a total topology of the kind of the different coordination polyhedra and their catenation. This set of contacts may be transposed into a Niggli-type connectivity formula[7] which depicts the coordination around the ions and the catenation of the respective polyhedra with other ones, i.e. the sharing of common corners, edges and faces, and this may be done for the partial structures as well as for the connectivity within the total lattice.

We again recur to the example of K_2NiF_4 to demonstrate the procedure. Given the coordination description as developed above, $K_2^{[9]}Ni^{[6]}F(1)_2^{[4+2]}F(2)_2^{[5+1]}$, we can describe the connectivity within the partial structure of the polyhedron around K by using the first numbers in the square brackets separately which give the ccs between K and F to formulate a Niggli-type connectivity formula for this part of the structure as: $[KF(1)_{4/4}F(2)_{5/5}]$. There are 8 K–F(1) contacts in all and 10 K–F(2) contacts which have to be split up among 2 K atoms. So, the first (numerator) part of the index gives the number of neighbours of this kind around K and the second (denominator) part indicates within how many polyhedra this species is shared. In a similar way the connectivity within the Ni–F partial structure is given as $[NiF(1)_{4/2}F(2)_{2/1}]$ since there are 4 Ni–F(1) and 2 Ni–F(2) contacts while the former anion is shared by two octahedra and the second one coordinates only one Ni ion. We at once have the typical picture in mind of the layer of corner sharing octahedra in this structure type. Figure 1 gives a presentation of this structure type where the partial structures are presented separately.

The true Niggli notation contains even more information to unambiguously describe a structure. It denotes also the way the ligands are shared between connected polyhedra by additional upper indices such as c(orner), e(dge and f(ace). Such information is unfortunately missing in our "Niggli-type" notations which we derive from the coordination number rule, so we can only make "intelligent" guesses using additional arguments such as the electrostatic repulsion (favouring corner vs. edge or even face sharing) or the increase of cell volume (which can be avoided by changing from corner to edge or even face sharing).

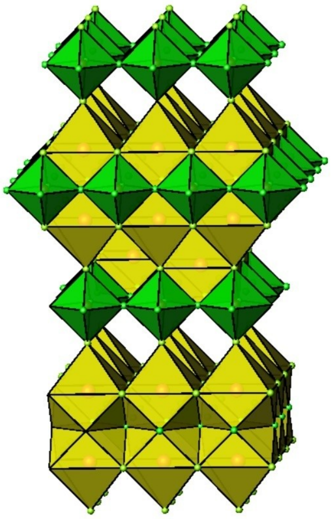

Figure 1. The structure of K_2NiF_4 showing the Ni–F– and the K–F partial structures in the upper and lower half respectively as well as the total catenation in the middle part. K polyhedra yellow, Ni polyhedra gree.

In a foregoing paper[6] we have presented this procedure of transformation to a Niggli-type connectivity notation in more detail. We have shown how even very complex notations of this kind may automatically be derived from the *a, b, c* and *p, q, r* values given in the formula for ternary compounds, and we have also shown how this works for binaries and quaternaries and for compounds with mixed anion types. We repeat a table given there which combines all this information in Table 1. An algorithm can easily be envisaged to deliver Niggli-type formulas from these inputs.

In this table we also show how connectivity formulas may be derived for so-called "reverse structures", i.e. with anion-centred polyhedra, which also give valuable insights into the topological system of a crystal structure. We have dwelled on this subject in more detail in the foregoing publication where we have also described how segregation mechanisms (see below) in the anionic sublattice can better be visualized. We will therefore not address this topic further in this paper. Figure 2 gives such a plot for our example.

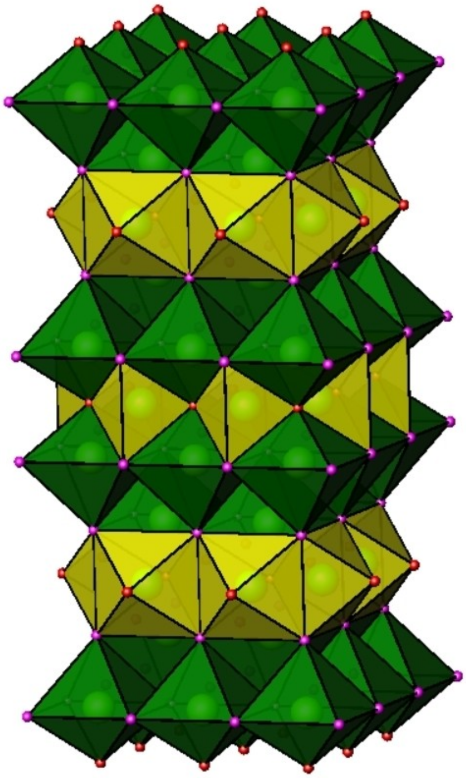

Figure 2. The "reverse structure" for K_2NiF_4, polyhedra around F(1) are given in yellow, those around F(2) in green.

Table 1. Development of coordination formulas and their extension to Niggli type connectivity notations.

Stoichiometry and “primary” coordination	Quaternaries $A_a^pB_b^qX_c^rY_d^s$	Binaries $A_a^pX_c^r$	Ternaries $A_a^pX_c^rY_d^s$	Ternaries $A_a^pB_b^qX_c^r$
Sum of ccs for cations/anions	$ap+bq=cr+ds$	$ap=cr$	$ap=cr+ds$	$ap+bq=cr$
ratio of contribution of the different constituents to the total of ccs	A: $ap/(ap+bq)$ B: $bq/(ap+bq)$ X: $cr/(cr+ds)$ Y: $ds/(cr+ds)$	A: ap X: cr	A: ap X: $cr/(cr+ds)$ Y: $ds/(cr+ds)$	A: $ap/(ap+bq)$ B: $bq/(ap+bq)$ X: cr
cc contribution of A, B, X, Y to *p, q, r, s*	The distribution of ccs among A, B, X, Y is not defined uniquely for such quaternaries.	r_A: ap/c p_X: cr/a	r_A: $(ap-ds)/c$ s_A: $(ap-cr)/d$ p_X: cr/a p_Y: ds/a	r_A: ap/c r_B: bq/c p_X: $(cr-bq)/a$ q_X: $(cr-ap)/b$
Example for the derivation of coordination formulas from incomplete information	A single missing parameter can be calculated by $ap+bq=cr+ds$. Only the mean of two stoichiometric indices or two coordination numbers can be calculated.	$A_a^pX_c^r\rightarrow$ $ap/c=r$ $A_a^pX_c^{ap/c}$	$A_a^pX_c^rY_d^s\rightarrow$ $(ap-cq)/d=s$ $A_a^pX_c^qY_d^{(ap-cq)/d}$ for unknown *q* accordingly	$A_a^pB_b^qX_c^r\rightarrow$ $(ap+bq)/c=r$ $A_a^pB_b^qX_c^{(ap+bq)/c}$
Niggli type notation for simple systems derived from: $A_a^{p_x+p_y}B_b^{q_x+q_y}X_c^{r_A+r_B}Y_d^{s_A+s_B}$		$A_a^pX_c^r$	$A_a^{p_x+p_y}X_c^rY_d^s$	$A_a^pB_b^qX_c^{r_A+r_B}$
for direct partial structures	$[AX_{((cr_A)/a)/r_A}Y_{((ds_A)/a)/s_A}]$ $[BX_{((cr_B)/b)/r_B}Y_{((ds_B)/b)/s_B}]$			$[A_{(cr_A/a)/r_A}]$ $[BX_{(cr_B/b)/r_B}]$
for reverse partial structures	$[XA_{(ap_x/c)/p_x}B_{(bq_x/c)/q_x}]$ $[YA_{(ap_y/d)/p_y}B_{(bq_y/d)/q_y}]$		$[XA_{(ap_x/c)/p_x}]$ $[YA_{(ap_y/d)/p_y}]$	$[XA_{(ap/c)/p}B_{(bp/c)/q}]$
for total direct structure	$[AX_{((cr_A)/a)/(r_A+r_B)}Y_{((ds_A)/a)/(s_A+s_B)}]_a$ $[BX_{((cr_B)/b)/(r_B+r_A)}Y_{((ds_B)/b)/(s_B+s_A)}]_b$	$[AX_{(cr/a)/r}]$	$[AX_{(cr/a)/r}Y_{(ds/a)/s}]$	$[AX_{(cr_A/a)/(r_A+r_B)}]$
for total reverse structure	$[XA_{(ap_x/c)/(p_x+p_y)}B_{(bq_x/c)/(q_x+q_y)}]_c$ $[YA_{(ap_y/d)/(p_x+p_y)}B_{(bq_y/d)/(q_x+q_y)}]_d$	$[XA_{(ap/c)/p}]$	$[XA_{(ap_x/c)/(p_x+p_y)}]_c$ $[YA_{(ap_y/d)/(p_x+p_y)}]_d$	$[XA_{(ap/c)/p}B_{(bp/c)/q}]$

We now see the two crystallographically different anions F(1) and F(2) coordinated by cations, the former having 4 K and 2 Ni atoms as neighbours and F(2) is in contact with 5 K and 1 Ni atom. We can again write out a Niggli-type formula $[F(1)K_{4/4}Ni_{2/4}]_2$ for the F(1) and $[F(2)K_{5/5}Ni_{1/2}]$ for the F(2) partial structure when keeping in mind that each K “belongs” also to 4 F(1) and 5 F(2) ions and Ni being neighbour to 4 F(1) and 2 F(2). By adding the denominators in the indices we arrive at the formula $[F(1)K_{4/9}Ni_{2/6}]_2[F(2)K_{5/9}Ni_{1/6}]_2$ for the total lattice. (As a test for such calculations we notice that the relation between atom pairs in such partial formulas is the reciprocal of the one in the corresponding formula of the “direct structure”.)

To end up this first part let us try and see whether this formal mathematical procedure could even help to predict possible structures or to anticipate at least certain features of their topology. We take a compound having the composition ABX_5 where we expect the cations to be sixfold coordinated. This will give $A^{[6]}B^{[6]}X_5^{[12/5]}$ in a first step which can be unravelled to $A^{[6]}B^{[6]}X(1)_2^{[3]}X(2)_3^{[2]}$, i.e. we need at least two different types[2] of anions to satisfy this combination of numbers. Now, X(2) can well have 1 A and 1 B around it, but X(1) will have $1^1/_2$ of each as neighbours. So, this example belongs to the category $r_A\in\mathbb{Z}$, $r_B\in\mathbb{Z}$ given in the first paragraph of this article. This can be represented by splitting up this anion type into two different ones of which one has [1 + 2] and the other one [2 + 1] A and B ions respectively in its coordination. So the total coordination formula would be: $A^{[6]}B^6X(1)^{[1+2]}X(2)^{[2+1]}X(3)_3^{[1+1]}$ and a Niggli-type formula for the partial structures would then be $[AX(1)X(2)_{2/2}X(3)_3]$ and $[BX(1)_{2/2}X(2)X(3)_3]$ giving a description for the total structure as $[AX(1)_{1/3}X(2)_{2/3}X(3)_{3/2}]$ $[BX(1)_{2/3}X(2)_{1/3}X(3)_{3/2}]$. We can “read” this formula by calculating the difference between the notation for the partial structures and that of the total structure showing us that both chains are connected closely as double chains. We can then depict this arrangement in an idealized form as given in Figure 3. (By the way, this is just the

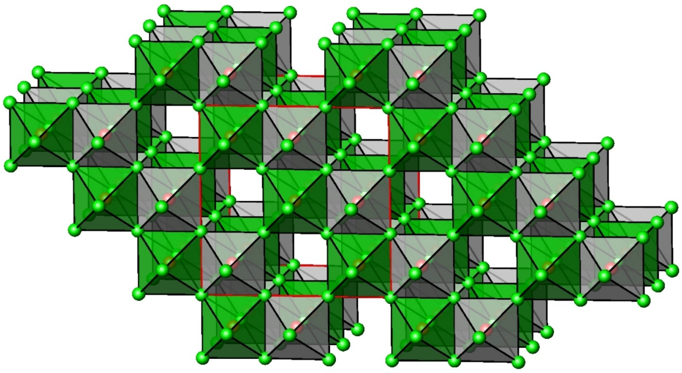

Figure 3. Idealized ABX_5 structure (see text), polyhedra around A grey, around B green.

topology found in one of the Nb_2O_5 polymorphs (R modification) where Nb formally Figures as A and B cation as well.)

So far, it seems possible to predict structures, we can at least develop a kind of algorithm to arrive at suitable topologies. However, we do not know whether this principle of simplicity will always be followed (see below) and – what is most important – we do not know the coordination numbers beforehand (see below). In the end we can rather discuss a "why" a posteriori than a "how" a priori!

Special cases ("Misfits")

The "numerical" solution given above results when we apply the procedure used so far – which we call "*the principle of simplicity*" – trying to use only adjacent integer numbers in balancing the number of coordination contacts (ccs) according to the stoichiometry of the compound, i.e. avoiding what we may call "segregation of the cations" (see below). There are many cases where this principle is violated and where "the scale of coordination numbers is spread". We take the structure of Cr_2F_5 as an example where Cr is in sixfold coordination but has two oxidation states, $Cr^{II}Cr^{III}{}_2F_5$. When looking at its structure we find a coordination notation as $Cr(1)^{[6]}Cr(2)^{[6]}F(1)_2^{[2+0]}F(2)^{[1+2]}F(3)_2^{[1+1]}$, and unravelling this notation in the same way we see why this "real" solution of the numerical problem is "better" (see Figure 4).

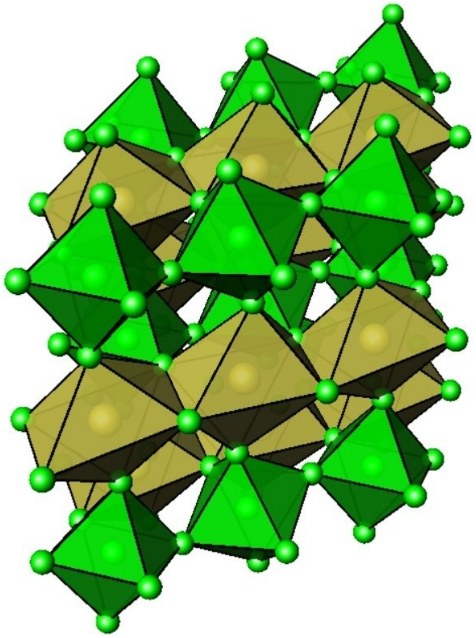

Figure 4. The structure of Cr_2F_5, polyhedra around Cr(1) green, around Cr(2) light brown.

In contrast to the "numerical" solution presented above for an ABX_5-type we see chains of $Cr(1)F_6$ moieties which are connected via corners and chains of $Cr(2)F_6$ octahedra connected via two opposite edges. The two types of chains are then connected by sharing corners. This avoids many short distances between the cations resulting in a weaker Cr^{II}–Cr^{III} repulsion within the cation substructure, and – what is even more important – it matches two kinds of octahedra with different size, a larger one around Cr^{2+} and the other one with Cr^{3+} in it by arranging the equatorial edge of the first kind of octahedra parallel to the diagonal of the other ones. Both "reasons" are the influence of other than purely mathematical needs. We will address them in the following as "chemical effects".

To make our point we may follow a series of such A_2X_5 compounds in comparing this structure with that of $CaCrF_5$ and $BaCrF_5$. In the former compound the coordination number of Ca is now 7 giving a "numerical" full co-ordination formula $Ca^{[7]}Cr^{[6]}F(1)^{[1+2]}F(2)_2^{[2+1]}F(3)_2^{[1+1]}$ which is just the one which we find for the real structure, the *"principle of simplicity"* holds in this case.

In the case of $Ba^{[12]}Cr^{[6]}F_5$ the coordination of the alkaline earth cation has again increased. The "numerical" solution for a co-ordination formula $Ba^{[12]}Cr^{[6]}F(1)^{[2+1]}F(2)^{[2+1]}F(3)^{[2+2]}F(4)^{[3+1]}F(5)^{[3+1]}$ is again different from that of the real structure, $Ba^{[12]}Cr^{[6]}F(1)^{[2+1]}F(2)^{[3+1]}F(3)^{[3+1]}F(4)^{[3+1]}F(5)^{[1+2]}$. In both cases there are chains of CrF_6 octahedra connected via opposite corners, but the large coordination polyhedra around Ba are connected differently via corners, edges and even faces (see Figure 5, partial structures at the sides, complete structure in the middle). We see that the connectivity of the polyhedra is smaller in the numerical case, and this would result in a much larger volume per formula unit. Again this may be termed as "chemical effect".

To give an intermediate summary we make a note of the fact that the numerical solutions derived from the general formulas $A_a^pB_b^qX_c^rY_d^s$ very often allow good guesses of at least parts of the structures. However, in some cases the real structures represent other possibilities of combining the numbers for *a, b, c, p, q* and *r* where the *principle of simplicity* is violated. In the following paragraphs we will deal with such "violations" and offer further explanations for them.

Segregation effects in crystal structures

The analysis of crystal structures in relation to the coordination number rule may also help to understand the reason for either a uniform distribution or a rather segregated one of different types of cations in an anion matrix.[8,9] To make our point we present the structures of $CaAs_2O_6$ and $FeNb_2O_6$ in comparison in Figure 6.

In $CaAs_2O_6$ there are alternating layers of CaO_6 and AsO_6 octahedra, the former being thinned out and separated and the latter arranged in zig-zag chains via edge sharing. The distribution in space is as homogeneous as possible according to the stoichiometric relation. In the structure of $FeNb_2O_6$ we find the minority component in zig-zag chains in one layer and the majority component in such chains within a double layer. Fe and Nb have clearly segregated into different sections within the structure.

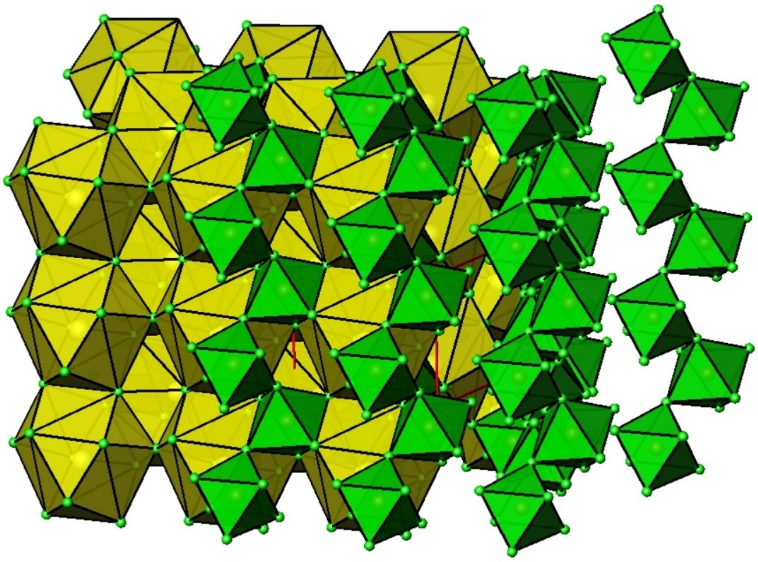

Figure 5. The structure of $BaCrF_5$, polyhedra around Ba yellow, around Cr green, left only Ba–F partial structure, right only Cr–F part.

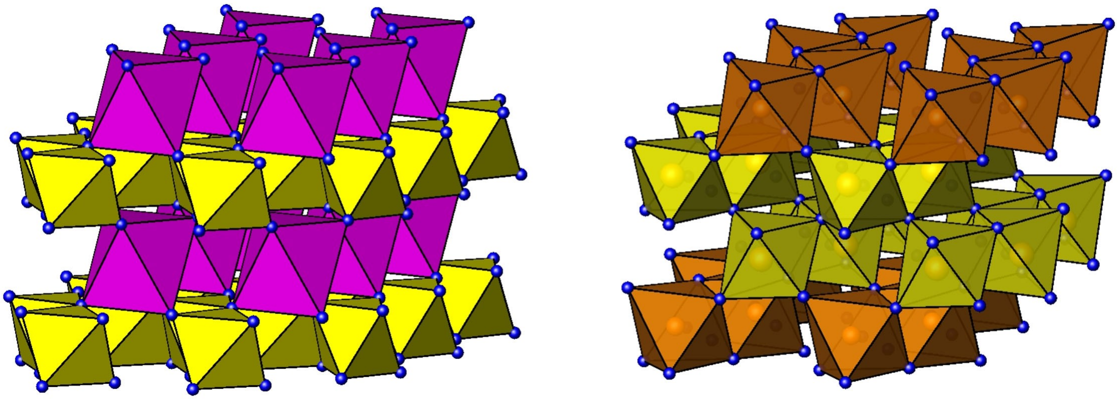

Figure 6. The structure of $CaAs_2O_6$ (left) and $FeNb_2O_6$ (right).

The coordination formulas for these compounds differ, $Ca^{[6]}As_2^{[6]}O_6^{[1+2]}$ and $Fe^{[6]}Nb_2^{[6]}O(1)_2^{[1+2]}O(2)_2^{[2+1]}O(3)_2^{[0+3]}$. The former complies well with what we would expect according to the rule of simplicity, r_A and $r_B \in \mathbb{Z}$ giving the simple numerical solution $X_c^{[r_A+r_B]}$, whereas the latter does not! The scale of numbers is spread beyond the adjacent ones for the O(3) anion which is the one connecting two layers of FeO_6 octahedra. In general, reducing r_A in $X_c^{[r_A+r_B]}$ means that the A cation "avoids" this anion type and by increasing r_B the cation B will "prefer" this anion as neighbour, this is a clear "segregation movement"! In Figures 7 we give other examples where the "segregation" into separate blocks is clearly seen, and the visual aspect is documented in a scientific notation in the coordination formulas. We will discuss possible reasons for such segregation effects in the following.

As said before, "spreading the scale" to realize the mean non integer r value will separate different cations within the anion matrix. This separation is evidently due to a partial "incompatibility of their chemical character" which may also be described as differences in bonding types. Coming back to our first example, K_2NiF_4, our chemical intuition tells us that interactions in the Ni–F partial structure may be different – more covalent – as compared to the more ionic ones between K and F, and the same is true for the other examples given above. Bi^{3+} with its lone pair character will tend to cluster within the oxide matrix, and the Mo–O moieties will tend to arrange as in most other sublattices in molybdates in the form of corner-sharing octahedra.

In order to approach a better understanding of such structural effects we have tried to quantify this "segregation" in a two-step procedure. We will show that a partial segregation may result not only from the "chemical facts" just mentioned but also already from the given combinations of the parameters a, b, c and p, q and r. We will call the latter a "numerical segregation Σ_{num}" and assign the term "chemical segregation Σ_{chem}" to the former aspect. A measure of segregation may be defined as

$$\Sigma = \sqrt{(1/z)\sum_{1}^{n} c_i[(\Delta r_{Ai})^2 + (\Delta r_{Bi})^2]}$$

where z is the number of formula units in the total formula, c_i is the number of equivalent anions of which there are n different sets. For our example $K_2^{[9]}Ni^{[6]}F(1)_2^{[4+2]}F(2)_2^{[5+1]}$ we find 2 different F-anions, F(1) and F(2), $n=2$, and each of them has the stoichiometric coefficient 2, $c_i=2$. The $\triangle$ values give the deviation of the actual individual coordination from the mean values (e.g. r_A and r_B in the case of ternary $A_aB_bX_c$ compounds). We use their squared values to include positive and negative deviations likewise and the root to reduce the values again. (For more details for the calculation see refs [6,9]). This is only one

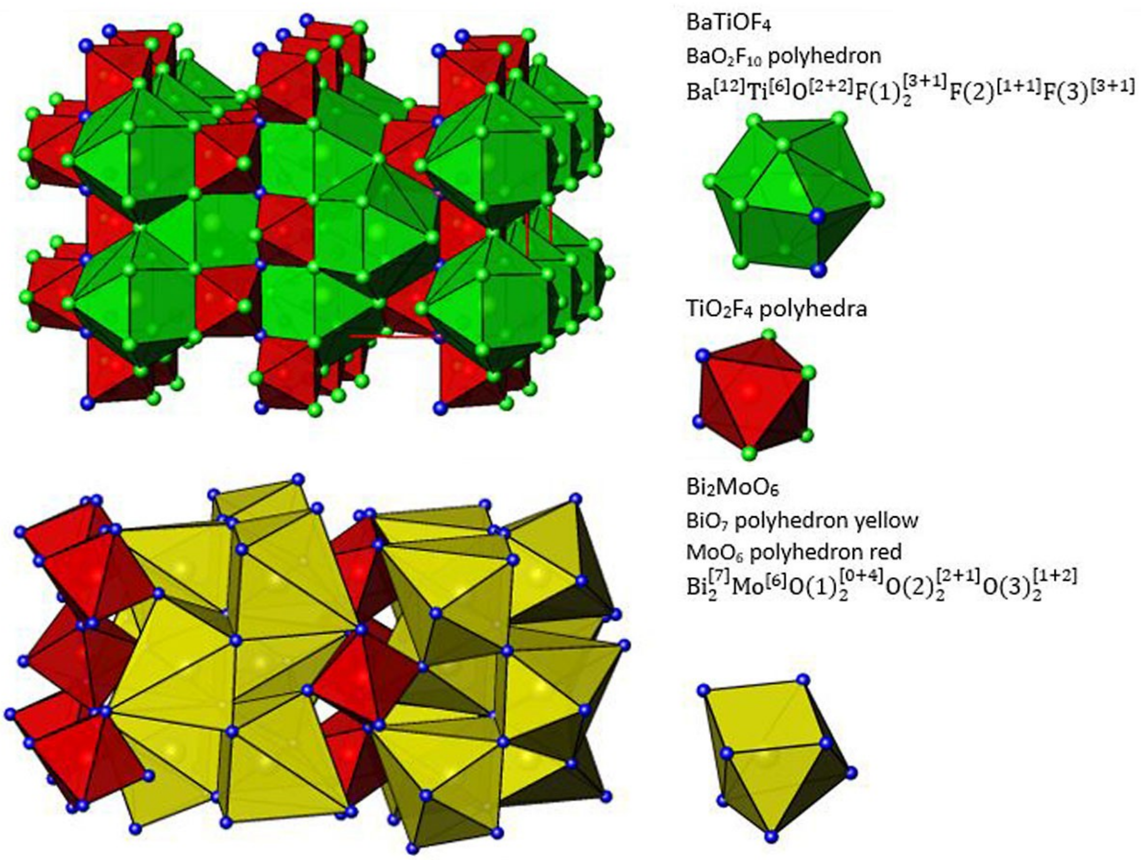

Figure 7. $BaTiOF_4$ (upper part) and $MoBi_2O_6$ (lower part) as examples for a "spread scale of coordination numbers".

approach of several others one may think of, but it offers a "scale", there is a "more" and a "less" to compare.

We come back to our first example where the coordination number rule may be written in a first step as $K_2^{[9]}Ni^{[6]}F_4^{[24/4]}$, i.e. $r_A = 18/4 = 4.5$ and $r_B = 6/4 = 1.5$. We have shown why this implies two different F anions giving the coordination formula $K_2^{[9]}Ni^{[6]}F(1)_2^{[4+2]}F(2)_2^{[5+1]}$. $r_{A'}$ for F(1) now amounts to 4 which is less than the average r_A ($\triangle r_A = -0.5$) and $r_{B'} = 2$, is more than the average r_B ($\triangle \mathrm{r_B} = +0.5$). The same calculations for F(2) give $\triangle r_A = +0.5$ and $\triangle \mathrm{r_B} = -0.5$. The number of formula units $z = 1$, and the numbers of equivalent anions F(1) and F(2) are both $c_i = 2$. Applying the formula given results in $\Sigma = 1.41$, so the simplest numerical solution following the rule of simplicity may already result in a segregation, we quantify it as Σ_{num}.

A similar calculation for $CaAs_2O_6$ will give $\Sigma = 0$ while that for $FeNb_2O_6$ results in $\Sigma = 2.83$, which is quite different though the cation coordination numbers are equal ([6]). We recall that following the rule of simplicity we arrive at the solution found for $CaAs_2O_6$ (where $\Sigma_{num} = 0$) and that the real structure of $FeNb_2O_6$ is different due to "chemical" driving forces. We therefore define this as Σ_{chem}. So, the segregation values found will be the sum of these two possible components and we define a total segregation as $\Sigma_{tot} = \Sigma_{num} + \Sigma_{chem}$. (A similar calculus for the example Cr_2F_5 discussed above with both Cr in [6] coordination is described by: $Cr(1)^{[6]}Cr(2)^{[6]}F(1)^{[2+0]}F(2)_2^{[1+2]}F(3)_2^{[1+1]}$ with 1.90 1.26 0.64 as $\Sigma_{tot,num,chem}$).

We may deepen this fundamental statement by a final example. For an AB_2O_6 compound where A is sixfold and B fivefold coordinated our general rule of simplicity results in the coordination formula $A^{[6]}B_2^{[5]}X(1)_4^{[1+2]}X(2)_2^{[1+1]}$ as "numerical simple solution". The segregation value calculated as given above yields $\Sigma_{num} = 1.15$. The compound CaV_2O_6 has just this combination of cation coordination numbers, however, the anion coordination is not as expected. We find $Ca^{[6]}V_2^5X(1)_2^{[1+1]}X(2)_2^{[2+1]}X(3)_2^{[0+3]}$ giving $\Sigma_{tot} = 3.06$.

We therefore distinguish between a total segregation and a numerical one and attribute the difference $\Sigma_{chem} = 1.91$ to „other than numerical contributions".

There are examples where:

$\Sigma_{num} = 0$ r_A and $r_B \in \mathbb{Z}$ giving the simple numerical solution $X_c^{[r_A + r_B]}$. The anion coordination numbers coincide with the r_A, r_B expected values.

$\Sigma_{num} = 0$ $r_A \in \mathbb{Z}$, $r_B \in \mathbb{Z}$ or $r_A \in \mathbb{Z}$, $r_B \in \mathbb{Z}$ or r_A, $r_B \in \mathbb{Z}$. Non-integer mean values r_A, r_B are "mimicked" by several integer ones.

$\Sigma_{chem} = 0$ The structure complies with the numerical "simple" solution.

$\Sigma_{chem} \neq 0$ There is segregation for other than numerical reasons.

In the following we venture to trace some further "non-numerical reasons".

Effects of electrostatic imbalance – thwarting Pauling's electrostatic rule

In 1929, Linus Pauling published a series of five empirical rules rationalising inorganic crystal structures.[10] They apply to ionic compounds and describe the preferred local environments of a cation and how these environments connect to each other. These rules have become a cornerstone of solid-state chemistry even though many examples have been found where they do not hold. So, they are rules but not laws of nature, they have nevertheless helped to rationalize crystal structures.

The second rule says: "In a stable coordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centres of the polyhedra of which it forms a corner". This rule has also been addressed in many papers during the ages since it was defined to show up deviations and possible extensions.[11,12] On the one hand it has helped to trace consequences of an "electrostatic misfit" in details of a structure leading to Baur's valuable rules[13] showing how distortions of chemical environments could compensate deviations from local charge sums. On the other hand, it has led to many puzzling comments in papers describing a newly found structure. Lately there has even been laborious statistical work to investigate the percentage of hits or fails on thousands of crystal structures.[14] Such tedious efforts seem unnecessary since an extension of the coordination number rule can clearly show why and what structural topologies cannot be balanced electrostatically according to Pauling's second rule. We will demonstrate this in the following passage.

We can define "values of electrostatic imbalance" (*Y*) quantifying the deviations of the formal ion charges of the anions from Pauling's electrostatic valence rule. We calculate such *Y* values in a similar was as the Σ values using the formula

$$Y = \sqrt{(1/z\,)\ \sum_{1}^{n} c_k[(\Delta r_k)^2]}$$

where again *z* is the number of formula units in the total formula, c_k is the number of equivalent anions of which there are *n* different sets, and the $\triangle$ values give the deviation of the actual valence sum around each anion from its formal valency (see above). We again use their squared values to include positive and negative deviations likewise and the root to reduce the values again. As for the Σ values we distinguish between a "numerical effect" and a "chemical" one by computing these values for the respective structure (Y_{tot}) and for the possible "simplest solution" where non-integer *r* values are matched only by a mean of neighbouring integer values for the coordination (Y_{num}). Y_{chem} is then again the difference between these two values.

We first recur to some examples which have already been used for our segregation studies. In $Ca^{[6]}As_2^{[6]}O_6^{[1+2]}$ all anions are surrounded by 1 Ca and 2 As offering 2/6 and 5/6 positive charge equivalents each respectively giving 12/6 in all. The structure is electrostatically balanced, $Y_{tot}=0$, i.e. $Y_{num}=Y_{chem}=0$. We remember that in this case $\Sigma_{tot}=\Sigma_{num}=\Sigma_{chem}=0$.

A similar analysis of $K_2^{[9]}Ni^{[6]}F(1)_2^{[4+2]}F(2)_2^{[5+1]}$ results in $Y_{tot}=Y_{num}=0.22$ and $Y_{chem}=0$. The slight imbalance is only due to the "awkward" numerical problem from the beginning on. $\Sigma_{tot}=\Sigma_{num}=1.41$

For $Fe^{[6]}Nb_2{}^{[6]}O(1)_2{}^{[1+2]}O(2)_2{}^{[2+1]}O(3)_2{}^{[0+3]}$ we find $Y_{tot}=1.0$, $Y_{num}=0$ and $Y_{chem}=1.0$. Here the imbalance is created by the segregation movement. $\Sigma_{tot}=\Sigma_{chem}=2.83$ and $\Sigma_{num}=0$

The third example is shown in Figure 8, $Ba^{[12]}Ti^{[6]}O^{[2+2]}F(1)_2^{[3+1]}F(2)^{[1+1]}F(3)^{[3+1]}$. We find the values $\Sigma_{tot}=1.99$, $\Sigma_{num}=1.41$, $\Sigma_{chem}=0.58$ and $Y_{tot}=0.47$, $Y_{num}=1.22$, $Y_{chem}=-0.75$. The additional "chemical" segregation beyond the numerical one has helped to reduce the electrostatic imbalance. We see that the minimization of electrostatic imbalance is a major driving force for "segregation movements". La_2MoO_6 (in its I-centred tetragonal modification modification) is another good representative for such a structural compensation of an otherwise large electrostatic imbalance. Its full formula is $La(1)_2^{[8]}La(2)_2^{[8]}Mo(1)^{[4]}Mo(2)^{[4]}O(1)_4^{[4+0]}O(2)_4^{[2+2]}O(3)_4^{[2+1]}$.

We show this structure in Figure 8. The segregation is quite extreme, $\Sigma_{tot}=6.66$, $\Sigma_{num}=2.67$, $\Sigma_{chem}=3.99$, starting with an unfavourable numerical solution further "chemical reasons" even aggravate the situation. But this helps to compensate an extreme electrostatic imbalance, $Y_{tot}=0.75$, $Y_{num}=2.44$, and Σ_{chem} is now even negative (-1.69).

We could extend this list by many examples, but the ones given here demonstrate all relevant cases and they also show relations between Σ and Y values.

We may summarize:

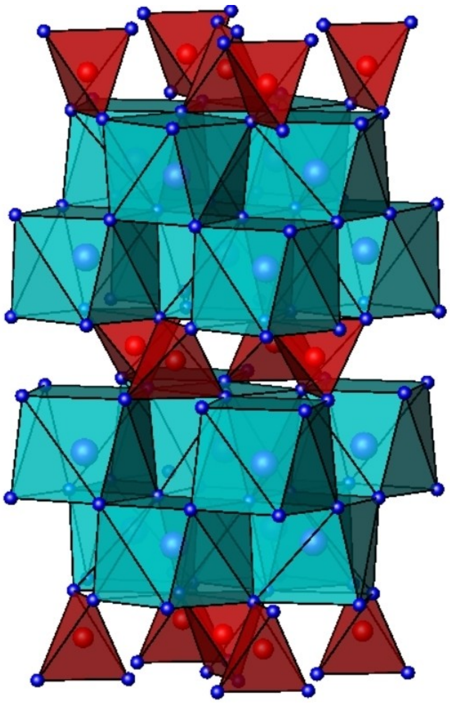

Figure 8. The structure of La_2MoO_6, sequence of layers along [001], La polyhedra light blue, Mo polyhedra red.

- We see that any of the Σ values marked as 0 will be mirrored alike in the concordant $Y=0$ value. We could even formulate another rule saying that *"ideal representations of the coordination need of the cations according to the numerical calculus without further clustering ($\Sigma_{chem}=0$) will result in a complete electrostatic balance in the structure"*. The opposite is not true.
- There are cases where a strong segregation (high Σ_{tot} value) more or less compensates the electrostatic imbalance of a "numerical solution" in the real structure.
- Negative Σ values are not possible by definition.
- In all cases where Σ_{tot} equals Σ_{num} there is no "chemically induced" electrostatic imbalance.
- Integer r values do not automatically give an electrostatic balance.
- The calculation of Y may result in negative values meaning that an electrostatic imbalance resulting from an unfavourable Σ_{num} and consequently large Y_{num} is at least partially "corrected by some segregation displacement".
- There are values which often occur (e.g. $\sqrt{2}$ and its multiples). This results from the mathematical definition of Σ an Y.
- The Y values depend necessarily on the charges of the ions. Therefore, they will be different for the same structure type but different ionic charges (e.g. K_2NiF_4 and Sr_2TiO_4). Dividing them by the charges would give values representative for a specific structure topology. However, keeping the different values for isotypic structures will better reflect the "internal tension" which will then relax more or less as described by the rules of Baur.
- The Σ values of compounds containing ns^2 cations are mostly large reflecting the fact that such cations tend to segregate in the structures leading to channels or layers where they accumulate. Nevertheless, except for rare cases, the Y values are still very moderate and Y_{chem} sometimes even negative indicating that the structural segregation does not go along with a strong electrostatic imbalance. It may even reduce it! The main effect of ns^2 cations is to increase the volume and the coordination number of these cations leading to the accordant catenation consequences.
- It is interesting to note that in polymorphic forms of the compounds those found at higher temperatures are more strongly segregated. The degree of clustering of like cations increases with the dilatation of the structures. However, this tendency is reversed when high temperatures induce a statistical distribution of different cations. The "individuality" of the cations is thereby blurred out by their thermal vibration, and the drive to segregate is weakened. Such effects are well understood in the application of Goldschmidt's rules describing the tendency of ions to substitute for other ones.

So, as said before, we should not "complain" that Pauling's electrostatic rule is violated in many cases and even try to "soothe the pain" by alluding to statistics to show how much hits are nevertheless found. Our calculus given here explains why it cannot hold for certain combinations of coordination numbers and stoichiometric coefficients. Such detailed studies of segregation coefficients in comparison with the electrostatic imbalance give valuable insights into the mechanisms of structural organisation. Baur's rules have shown how local "movements" decrease the electrostatic imbalance by adjusting bond lengths according to different coordination numbers. Our approach adds a further important fact, it shows how a complete topological reorganisation helps to avoid an otherwise too large electrostatic imbalance.

Conclusion

The coordination number rule expresses the very trivial fact that the number of coordination contacts (cc) of the cations equals those of the anions. There are corollaries of this statement such as *"the ratio of the average coordination number of the cations to the average coordination number of the anions is the same as the ratio of the number of anions to the number of cations"* and another one saying: *"compounds with high anion content will stabilize high cation coordination numbers"*. This implies that stoichiometric relations play a decisive role. In our teaching we often recur to sizes as main cause for the formation of a specific coordination, and we even discuss structure field diagrams showing the stability fields of certain structure types in relation to ion sizes.

However, seeming "sizes" of the ions in a structure are never fixed properties, they depend on the type of interacting components in a structure and on the stoichiometric relations. They cannot be looked up in tables! We can exemplify this important fact by the plot of coordination numbers found in a set of potassium titanates (Figure 9). Depending on its "stoichiometric weight" the coordination numbers of the K ion will range from above 10 down to 4 in K_2O, and the type of counterions will furthermore play a decisive role. (In this plot it does makes sense to use "effective coordination numbers" as described by Hoppe and others. I repeat that we don't do so when applying the coordination number rule where only integer numbers are possible.)

An analysis of crystal structures in the light of the coordination number rule as presented here in a refined approach gives insight into very complex structural arrangements. We have mostly taken ternary compounds $A_a^{[p]}B_b^{[q]}X_c^{[r]}$ as examples where we can show the outcome of this rule better than for binary or even quaternary compounds where we arrive either at simpler statements or where the result is sometimes ambiguous as in the latter case (see Table 1). We have shown how the rule $ap+bq=cr$ and the contribution of the different cations to the coordination of the anions is given by $r=r_A+r_B$, where $r_A=ap/c$ and $r_B=bq/c$, "is mapped into" the topology of a crystal structure. A crucial point comes up when r_A and/or r_B, which are both a mean coordination number of the anions, are not integers. Since coordination numbers must be integers in this topological approach, we can mimic non-integer mean coordination numbers by an average of some other integers leading to several crystallographically different anions. This average may be produced by diverse combinations of integers. However, we have first chosen to follow another main principle of structural chemistry, the principle of simplicity where we form such averages by using only adjoining integers. This will tend to make at least similar surroundings for all participants in the game of neighbourhood and therefore also helps to approach the principle of maximal symmetry which has long been upheld as a decisive factor of structure formation.[15–17] We have termed such constellations as "numerical solutions" and have explained the ones deviating from such principles as driven by "chemical effects". Moving away from adjoining integers will forcibly lead to some segregation effects, one anion type being "preferred" by one kind of cation and the other loosing this kind of neighbourhood. There is much chemical sense also in such solutions of the numerical problem. In such ternary systems (and of course even more in any multinary one) we combine several cationic (or anionic) species with quite different "properties" such as redox potential, electropositivity or electronegativity, charge or general electron

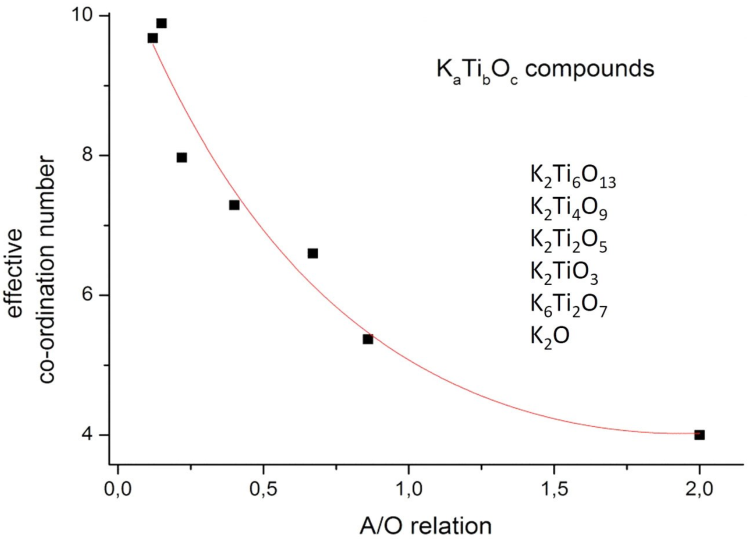

Figure 9. Coordination numbers for K in a series of K-titanates.

density, more ionic or covalent "character" and so on in one stable compound. They will forcibly tend to separate when they differ too much in such properties, and this is realized just by breaking this principle of simplest numerical solution or maximum symmetry. We have also addressed the principle of electrostatic balance as a driving force for creating a topology more or less way off from these principles and could thereby "reconcile" with the "violations" of Pauling's electrostatic rule.

Summarizing we can say that an analysis of structures in the light of the coordination rule can help to rationalize even very complex crystal structures. Findings of other authors also prove that the crystal chemical indicators presented along this coordination number rule are very useful tools in crystal chemistry even beyond typical ionic compounds such as oxides and fluorides. They have been applied successfully also to structures of hydride compounds.[18] The crystal structures obey these rules even in complex transition-metal hydrides where bonds are considered to be mainly covalent, and the notion of ion segregation and electrostatic imbalance can nicely explain the observed structures. Furthermore, we may even use them – to a certain extent – as a tool to predict structures or at least important features of them once we have clear indications how to choose coordination numbers of the component atoms. Future work should focus on finding a way to complete the Niggli-notations by the missing indices as mentioned above which will then define the catenation of all polyhedra in a definite way and lead to good predictions of structures. We doubt that ML or KI approaches will be successful to further develop these ideas. They could create perhaps large "toolboxes" containing many possible structural configurations among which to choose in view of further parameters defining the optimal arrangement of atoms in a given compound. A comparison of formation energies from quantum chemical calculations may then decide the game in the end.

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Conflict of Interest

The authors declare no conflict of interest.

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