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The classification of 1D ‘perovskites’

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There has been a huge amount of interest in perovskites recently and new structures of hybrid perovskites are frequently reported. The classification of perovskites has been unambiguous in the discussion of 3D and layered 2D perovskites due to the dimensional constraints. However, in 1D perovskites, the additional degrees of freedom have resulted in a large number of possible structural configurations. The new proposed notation aims to classify these structures based on the connectivity of the octahedra of the perovskite, which has a periodic repeating pattern. However, the notation should be restricted to simple 1D perovskites and haloplumbate structures as the notation would become too cumbersome when applied to an exotic framework which has 3D characteristics, such as perovskite polytypes.

1. Introduction

With the rising number of reported 1D hybrid perovskite structures, there has been a wide variety of names given to these structures, ranging from ‘one-dimensional perovskite’ (Yuan *et al.*, 2017; Seth *et al.*, 2019), ‘zigzag edge-sharing perovskite’ (Jung, 2020), ‘double-chain one-dimensional perovskite’ (Jodlowski *et al.*, 2016), ‘face-sharing polytype’ (Stoumpos *et al.*, 2017), ‘plumbate chains’ (Febriansyah *et al.*, 2020) to ‘perovskitoid’ (Stoumpos *et al.*, 2017; Li *et al.*, 2020). For the 3D and 2D perovskite structures, there have been several naming conventions which are widely used for oxide perovskites. In 3D perovskite systems, this includes polytypism, and the commonly used notations are the Ramsdell (1947) and Gard (Guinier *et al.*, 1984) notations. In 2D layered perovskites, this would include Ruddlesden–Popper, Dion Jacobson and Aurivillius phases, each having their own defining trait. More recently, there is the ‘alternating cation in interlayer space’ (Soe *et al.*, 2017) system, which is observed only in hybrid perovskites. While Stoumpos *et al.* (2017) first introduced ‘perovskitoids’ as having exclusively face-sharing connectivity between the $[MI_6]^{4-}$ octahedra, the term ‘perovskitoids’ was later broadened to include materials with edge- and face-sharing connectivity (Li *et al.*, 2020). Although such structures have traditionally been classified as plumbates, the definition remains vague and does not capture the periodicity effect of the connectivity of the lead halide octahedra. With the three variants of connectivity, namely, corner, edge and face sharing, there is an almost infinite number of combinations which could result in such a 1D chain, all of which result in an apparent ‘nanowire’ configuration, yet each structure is distinct. This article proposes a new nomenclature and notation for 1D perovskites, ‘perovskitoids’ and plumbates.

2. The proposed notation: reduced notation and extended notation

When considering these 1D ‘perovskitoid’ structures, three main parameters are required to describe the structural connectivity: the intralayer periodicity, connectivity within the repeating unit and, lastly, the connectivity to the next repeating unit. These could be used to produce a new way to describe 1D structures. However, it should be noted that while this proposed notation can also be applicable to 2D and 3D structures, it would take on a rather awkward form (as shown in §2.2), and hence, where applicable, the more established Ramsdell or modified Gard notation should continue to be utilized for such materials. It should also be noted that in the derivation of this notation, all octahedra are idealized, as octahedral distortion and tilting would be beyond the scope and objective of the proposed notation.

All the corners, edges and faces of an ideal octahedron are first defined as shown in Fig. 1. All six corners would be labelled with the italicized numeral *1* to *6*, but it should be noted that the face of an octahedron should not be confused with the Miller indices. When any corner, edge or face is defined, the lowest number combination should be taken as the reference point.

With all vertices of an octahedron defined, we can now move onto the connectivity and repeat unit of such 1D structures. Each layer would be perpendicular to the direction of the 1D chain connectivity. First, the main parameter to consider is the number of octahedra per layer. If there is more than one octahedron per layer, the intra-layer connectivity would also have to be defined in parentheses. Special considerations, for example, cyclic connectivity, should also be included in this section if it arises from the intra-layer connectivity. In the examples analysed, however, no such special considerations are observed.

The second parameter would be the number of layers of octahedra required for the stacking or connectivity sequence to repeat itself. If there is more than one octahedron per repeat of the stacking sequence, the connectivity type should be specified: F for face sharing, E for edge sharing and C for corner sharing. The last parameter pertains to the connectivity to the repeating sequence, with again F, E and C denoting face, edge and corner sharing, respectively, or X, for no connectivity. Although materials having no connectivity would

Figure 1

A schematic showing the naming convention for labelling all six corners, with highlighting for (a) corner *1*, (b) edge *12* and (c) face *125* of an octahedron.

1-2 F₃₄₆ F₃₄₆, (1-2FF)

Figure 2

The structure shown here has one octahedron per layer and the repeating unit has two layers where the octahedra are connected through face sharing. The repeating unit is connected to the next unit through face sharing. The structure illustrated here is taken from *catena*-(2-methylimidazo[1,5-*a*]pyridin-2-ium tris(μ -bromo)lead) (Skelton *et al.*, 2019), with the organic ligands not shown for clarity. Notably, other structures like 1-4FFFF and 1-6FFFFFF are isostructural, and can be simplified to 1-2FF when the octahedra are idealized. The extended notation of this structure would be 1-2 F₃₄₆ F₃₄₆.

strictly speaking not be a 1D ‘perovskitoid’, such a naming framework would also help to describe similar systems for easy comparison. At this point, it should be obvious that if there is one octahedron per layer and *n* octahedra making up the repeating unit, there would be a connectivity of *n*. In instances where the connectivity involves only corner sharing, corner 5 should point in an arbitrary upwards direction and corner 6 in an arbitrary downwards direction perpendicular to the propagation of the 1D chain. This condition is imposed to restrict any ambiguity arising from the rotational freedom.

Thereafter, one should identify the repeating pattern in the unit cell first, then shift the ‘origin’ such that the naming priority would be given for corner sharing over edge sharing over face sharing over no connectivity, *i.e.* C > E > F > X. Subsequently, the notation would be reduced to the simplest repeating pattern without including the effects of crystallographically inequivalent B-site cations (see example on 1-2FF; Fig. 2). Hence, this proposed naming convention, also called the reduced notation, is separated into two parts, each defining the afore-mentioned parameters. It would take a general form of (number, intralayer connectivity if any) – (number, interlayer connectivity).

It should be emphasized here that it is the objective of this notation to be kept simple for even noncrystallographers to utilize with ease. However, the limitation of this notation can be seen with certain configurations, such as 1-2EE (Figs. 3

Figure 3

The structure shown here has one octahedron per layer and the repeating unit has two layers, where the octahedra are connected through edge sharing. The repeating unit is connected to the next repeating unit through an equivalent edge and hence takes the reduced notation 1-2EE or the extended notation $1-2 E_{14} E_{32}$. The structure is taken from $C_4N_2H_{14}PbBr_4$ (Yuan *et al.*, 2017).

and 4), which can exhibit ‘isomerism’ through different edge connectivity. Therefore, a full notation which can be simplified to an extended notation is designed to address this limitation.

A small difference between the full and extended notation will be discussed here. The full notation would show the preceding referenced octahedra corner or edge or face superscripted on the left of the connectivity label and the following connectivity of the referenced octahedra corner or

edge or face subscripted to the right, and would take the general form $^{XYZ}A_{X'Y'Z'}$. According to the earlier definition where the referenced corner, edge or face would have the lowest number combination, the second octahedron in the first repeating unit would always be referenced on corner 1 or edge 12 or face 125. By virtue of repeating this naming convention to the first octahedron in the second repeating unit, the first octahedron would therefore also be referenced on corner 1 or edge 12 or face 125. Therefore, the preceding reference in superscript (*i.e.* the subscript XYZ) can be dropped since it can only be 1, 12 or 125 for a corner, edge or face shared octahedron. In doing so, we would obtain the extended notation which has a general form of $A_{X'Y'Z'}$. Consequently, the order of the numbering would also be meaningful where $1-2^{X1Y1Z1}F_{X1'Y1'Z1'}^{X2Y2Z2}F_{X2'Y2'Z2'}$ and $1-2^{X3Y3Z3}F_{X3'Z3'Y3'}^{X4Y4Z4}F_{X4'Z4'Y4'}$ convey different meanings; the former would mean that the face connectivity between the first and second octahedra is oriented such that corner $X1'$ matches with $X2$, corner $Y1'$ matches with $Y2$ and corner $Z1'$ matches with $Z2$, while the latter would mean the face connectivity happens where corner $X3'$ matches with $X4$, corner $Z3'$ matches with $Y4$ and corner $Y3'$ matches with $Z4$. Such specificity would remove any potential room for ambiguity. During instances where the preceding connectivity would not be 1, 12 or 125, or if the structure is connected in a highly novel way, it is recommended to utilize the full notation instead. It should be noted that for X connectivity, the syntax would be slightly different for the reduced and extended notations. Taking the example of a system which has an extended notation of $1-3^X F_{435} F_{346} F_X$, the reduced notation is written as 1-3FFX instead of 1-3FFF or $1-3FFF_X$. This is necessary because the X connectivity must be present in the reduced notation to convey the meaning of no connectivity beyond the third octahedron, and it is the nature of the reduced notation to only show the connectivity style. 1-3FFF would convey the meaning of a full continuous 1D chain of face-sharing octahedra, and $1-3FFF_X$ would have gone beyond the very definition of the reduced notation. At the same time, the extended notation can be read as: ‘there is one octahedron in one layer, three layers form the repeating unit (and hence three octa-

Figure 4

The structure shown here has one octahedron per layer and has two octahedra per repeating unit which are connected through an edge. The connectivity of the octahedra here is distinct from that in Fig. 3, even though this structure also has a reduced notation of 1-2EE. The extended notation of this structure is written as $1-2 E_{53} E_{63}$, which shows the difference in the edges through which the octahedra are connected. The structure is taken from $(H_2Bpy)PbBr_4$ (Liu *et al.*, 2019).

Figure 5

The structure shown here has one octahedron per layer and the repeating unit only has one layer. The repeating unit is connected to the next unit through a corner-shared halide and hence takes the notation 1-1C or the extended notation 1-1 C_3 . The structure is taken from $[C_3N_6H_8]_2PbCl_5 \cdot Cl$ (Hamdi *et al.*, 2018).

hedra form each repeating unit), where the reference corner 1, edge 12 and face 125 of the first octahedron is not connected to anything, face 435 of the first octahedron is connected to face 125 of the second octahedron and face 346 of the second octahedron is connected to face 125 of the third octahedron. There is no further connectivity beyond the third octahedron'. When there is more than one way of writing the connectivity, the sum of the numbers with the smallest combination should be used (see 1-1C, Fig. 5). If the sum of the numbers is equal, then the combination with the most instances of the smallest number would be used (see 1-2EE, Fig. 4). In another unusual instance of more than one connectivity from the same layer, underlining would be used to specify which corner or edges are being referred to for the subsequent connectivity (see Fig. 6 and Fig. S4 of the supporting information). Furthermore, the use of an arbitrary '+' and '-' is also introduced in §2.2 (see Figs. 6 and 7), but if the structure is also connected perpendicular to the direction of propagation of the 1D structure, the result is not likely to be a 1D structure and this proposed notation should not be used to describe the structure if another chemical naming convention exists.

Figure 6

The structure of a 3D network of 1-6F(CC)FF(CC)F, which is rewritten as 1-6(CC)FF(CC)FF. In full notation, the structure will be written in a highly awkward form, 1-6 ($\overset{1+}{C}_{435}$ $\overset{1-}{C}_{325}$) $\overset{125}{F}_{346}$ $\overset{125}{F}_{3-4+}$ ($\overset{1+}{C}_{346}$ $\overset{1-}{C}_{236}$) $\overset{125}{F}_{346}$ $\overset{125}{F}_{3-4+}$. The '+' sign and '-' sign specify the arbitrary positive direction and the underlining would specify which octahedron the subsequent connection would be based. The structure here is taken from $\{(C_9H_{14}N)_4[Pb_3I_{10}]\}_n$ (Billing & Lemmerer, 2006).

2.1. Examples of connectivity

After looking through over 1200 lead halide examples in the Cambridge Structural Database (CSD; Groom *et al.*, 2016), aided by *ConQuest*, 20 different configurations were observed, of which the eight most frequently observed are summarized here and the remaining configurations can be found in the supporting information. The list is by no means exhaustive but does highlight that certain types of connectivity are more

Figure 7

The corrugated ring structure formed by six pairs of face-shared octahedra, where the arrangement of the dimers is alternating and, hence, only three are seen in the first layer and three in the second layer. The two layers are related through a 6_1 screw axis and form a cyclic ring only across two layers. The repeating unit is then connected to the next repeating unit by a 6_1 screw axis with six corner-shared octahedra. Hence, this system would be $\text{cyclo}[3(2F)-2(6_1\text{CCCCC})]6_1\text{CCCCC}$ or in the full notation, would also take on a highly awkward form of $\text{cyclo}[3(2 \overset{x}{F}_{346} \overset{125}{F}_x)-2(6_1 \overset{6+}{C}_1 \overset{3-}{C}_5 \overset{6+}{C}_1 \overset{3-}{C}_5 \overset{6+}{C}_1 \overset{3-}{C}_5)](6_1 \overset{6+}{C}_1 \overset{3-}{C}_5 \overset{6+}{C}_1 \overset{3-}{C}_5 \overset{6+}{C}_1 \overset{3-}{C}_5)$. Hence, the proposed notation should be avoided altogether in this structure. The structure is taken from $(\text{HMTA})_3\text{PbBr}_7$ (Lin *et al.*, 2017).

Figure 8

The structure shown here has one octahedron per layer and the repeating unit has three layers within the unit cell with the octahedra sharing in the order of face, edge and face sharing. With the order of priority of edge sharing over face sharing, this sequence is rewritten as edge, face and face sharing, and thus takes on the reduced notation 1-3EFF or the extended notation $1-3 E_{435} F_{346} F_{34}$. The structure illustrated here is $(C_{12}N_2H_{14})_2Pb_7Br_{18}$ taken from Liu *et al.* (2016), with the organic ligands not shown for clarity.

prominent. In this first example, the octahedra of the 1D chain are all connected only through face sharing. Hence, in the reduced notation it can be written as 1-2FF. Notably, there are several systems which demonstrate crystallographically distinct octahedra, even though the connectivity closely resembles 1-2FF, such as 1-4FFFF and 1-6FFFFF, where the main difference is observed when looking along the 'nanowire' axis of propagation. However, in an idealized octahedron, such connectivity can be simplified to 1-2FF and the crystallographically inequivalent B-site cations in 1-4FFFF and 1-6FFFFF are the result of a distorted octahedron. Accord-

ing to the rule where the repeating units are first taken from the unit cell (e.g. four octahedra for 1-4FFFF), the notation would then be reduced to the simplest repeating unit, without considering the effects of a crystallographically distinct central B-site cation, which will be 1-2FF. This structure has a repeating unit with one octahedron per layer, and it has two layers per repeating unit. The octahedra are then connected through face sharing. Each repeating unit is then connected to the next repeating unit through face sharing, taking on the notation 1-2FF. In the full notation, this will be written as $1-2^{125}F_{346}^{125}F_{346}$. As can be seen here, the superscripted 125 is redundant and, thus, the full notation can be simplified as the extended notation $1-2 F_{346} F_{346}$.

This configuration was seen to be the most common connectivity among such 1D plumbate structures. In a search through the CSD for only Pb–Br- and Pb–I-based structures, around 190 unique compounds were found to take on this connectivity. Some well-known examples include 1-ethylpyridin-1-ium bromide (Febriansyah *et al.*, 2020), 1-benzylpyridin-1-ium iodide (Febriansyah *et al.*, 2020) and imidazolium lead iodide (Arora *et al.*, 2019).

The second most commonly observed connectivity is 1-3EFF (Fig. 8). This structure has one octahedron per layer, and it can be seen from the unit cell that there are three octahedra which form the repeating unit. From Fig. 8, the connectivity of face, edge and face can be seen within the unit cell, which would give us the reduced notation 1-3FEF. Since priority is given as $C > E > F > X$, this would be rewritten as 1-3EFF. In the full notation, it will be written as $1-3^{12}E_{435}^{125}F_{346}^{125}F_{34}$, which can be reduced to $1-3 E_{435} F_{346} F_{34}$. From the full notation, it can be read that the first octahedron has a preceding connectivity from edge 12, connected to the second octahedron through face 345. The second octahedron is connected to the first octahedron through face 125 and with the third octahedron through face 346. The third octahedron is connected to the second octahedron through face 125 and the fourth octahedron (*i.e.* the first octahedron in the next repeating unit) through edge 34. It should also be noted that the order of the numbering for the edges, and especially for

Figure 9

The structure shown here has one octahedron per layer and the repeating unit has three layers where the octahedra are connected through face sharing. The repeating unit is not connected to the next unit and hence takes the notation 1-3FFX or the extended notation $1-3^X E_{435} F_{346} F_X$. The structure is taken from $[Me_3TPT]_2[Pb_3Br_{12}] \cdot 6H_2O$ (Pan *et al.*, 2017), with the organic ligands not shown for clarity.

the faces, does matter. In this example, it would mean that face 346 of the second octahedron is shared with face 125 of the third octahedron, where corner 3 of the second octahedron matches with corner 1 of the third octahedron, corner 4 of the second octahedron matches with corner 2 of the third octahedron and corner 6 of the second octahedron matches with corner 5 of the third octahedron. Again, it can be seen that in a 1D chain, by definition, the preceding connectivity will always be ^{125}E or ^{125}F or ^1C ; thus, the extended notation of 1-3EFF would be $1-3\text{E}_{435}\text{F}_{346}\text{F}_{34}$.

The next example seen in Fig. 9 demonstrates the relevance of the proposed notation when the connectivity does not form a continuous chain. In this configuration, there is one octahedron per layer and the repeat unit consists of three layers. Within the repeating unit, the octahedra are all connected through face sharing, similar to 1-2FF. However, each repeating unit, which consists of three octahedra, does not connect to the next and thus they form mini-rods of three face-connected octahedra. Hence, such connectivity would be written as 1-3FFX (Fig. 9) in the reduced notation or have the extended notation $1-3\text{F}_{435}\text{F}_{346}\text{F}_X$.

The following structure seen in Fig. 5 shown would be the only true 1D perovskite structure in the list. In a perovskite structure, all lead halide octahedra are corner shared to form a large 3D network. In a 1D perovskite structure, the connectivity is now restricted to connectivity along one direction. For such connectivity, there is one octahedron per layer and one repeating unit which are all corner connected. As such, this would take the reduced notation 1-1C or the extended notation $1-1\text{C}_3$.

The following example on 1-2EE shows the main limitation of the reduced notation, where the same notation can give rise to more than one unique structure, which is similar to isomerism. Hence, the extended notation or even the full notation is necessary here to give a clear definition. In Figs. 3 and 4, there is one octahedron per layer, and it takes two octahedra for the pattern to repeat into a 1D chain. However, the connectivity is distinct in the two structures. By the earlier defined edges of an octahedron, the extended notation for the structure shown in Fig. 3 is written as $1-2\text{E}_{32}\text{E}_{14}$, whereas the structure in Fig. 4 is written as $1-2\text{E}_{53}\text{E}_{63}$. It should be noted that the structure in Fig. 4 can be written in several different forms, such as $1-2\text{E}_{35}\text{E}_{56}$ or $1-2\text{E}_{53}\text{E}_{54}$, but these forms are less preferred. $1-2\text{E}_{35}\text{E}_{56}$ is not preferred because the sum of the numbers is larger (*i.e.* $5 + 3 + 6 + 3 < 3 + 5 + 5 + 6$), while $1-2\text{E}_{53}\text{E}_{54}$ is less preferred because the smallest number (*i.e.* 3) is more highly used in $1-2\text{E}_{53}\text{E}_{63}$. Notably, the difference between $1-2\text{E}_{53}\text{E}_{54}$ and $1-2\text{E}_{53}\text{E}_{63}$ arises from which octahedron the series starts from, and it is shown in Fig. S21 (see supporting information) that by shifting the reference octahedron by one unit, both structures can be superimposed on each other. The notation proposed here would thus, hopefully, help to guide further discussion on the effects of the significance of the sharing of octahedra in these ‘perovskitoids’ by allowing comparisons of the connectivity through the reduced notation, and a further level of insight when the structures have the same type of connectivity but are structurally

different, which can be seen through the extended or full notation.

From the list of haloplumbates screened through the CSD, the example shown here is the only configuration which has more than one octahedron per layer. In each layer, there are two lead halide octahedra connected through an edge and there is only one repeating layer. The terminal octahedra are connected to the next unit through corner sharing. Hence, such connectivity would be labelled 2E-1(CC) (Fig. 10). Since C has a higher priority over E, the reference corner 1 would be based on the corner which is connected to the preceding layer. Hence, this structure will take on a full notation of $2\text{E}_{52}^{25}\text{E}_X - 1(^1\text{C}_3\text{C}_3)$, which can be simplified to the extended notation $2\text{E}_{52}^{25}\text{E}_X - 1(\text{C}_3\text{C}_3)$ by dropping the reference corner 1.

In the next example, seen in Fig. 11, the terminal connectivity is *via* two corner-shared octahedra. There is one octahedron per layer and two corner-shared octahedra form the repeating unit. The octahedra are connected through corner sharing to form a zigzag 1D chain. Thus, this structure would have a reduced notation of 1-2CC (Fig. 11) or the full notation $1-2\text{C}_2\text{C}_4$, which can then be reduced to $1-2\text{C}_2\text{C}_4$.

2.2. Failure when extended to other systems

While it would be tempting to extend this notation to include other larger 2D networks, the notation would take on an awkward form, exposing the main limitation of the proposed notation.

Based on the unit cell, this structure can be seen as 1-6F(CC)FF(CC)F and, based on the octahedral sharing priority rule, would be rewritten as 1-6(CC)FF(CC)FF (Fig. 6). In the full notation, taking the *c* axis as pointing ‘up’ (*i.e.* octahedral corner 5), it will be written as $1-6(^1\text{C}_{435}\text{C}_{325})^{125}\text{F}_{346}\text{F}_{3,4} (^1\text{C}_{346}\text{C}_{236})^{125}\text{F}_{346}\text{F}_{3,4}$. It can be seen here that the notation is on the verge of breaking down because the two-corner-shared octahedron is accompanied by a displace-

Figure 10

The structure shown here has two octahedra per layer, which are connected through edge sharing, and the repeating unit only has one layer. Each repeating unit is connected to the next repeating unit through corner sharing and hence this takes the reduced notation 2E-1(CC) or $2\text{E}_{52}^{25}\text{E}_X - 1(^1\text{C}_3\text{C}_3)$ in the extended notation. The structure illustrated here is taken from $(\text{C}_{10}\text{H}_{12}\text{N}_2)_2[\text{Pb}_2\text{Br}_8]$ (Ali *et al.*, 2007).

Figure 11

The structure shown here has one octahedron per layer and the repeating unit has two layers where the octahedra are connected through corner sharing. The repeating unit is connected to the next repeating unit through corner sharing and hence takes the notation 1-2CC or the reduced notation 1-2 C₂ C₄. The structure is illustrated here is taken from [(CH₃)₂CHNH₃]₃PbI₅ (Hartono *et al.*, 2019).

ment in the $\pm b$ axis. Even with a slight modification, by including '+' for displacement in the positive b axis and '-' for displacement in the negative b axis, as well as underlining the octahedron to specify that the subsequent connections are based on the underlined octahedron, the full notation would be 1-6 (¹⁺C₄₃₅ ¹⁻C₃₂₅) ¹²⁵F₃₄₆ ¹²⁵F_{3,4+} (¹⁺C₃₄₆ ¹⁻C₂₃₆) ¹²⁵F₃₄₆ ¹²⁵F_{3,4+}. Similarly, for 1-3(CC)FF (Fig. S9 in the supporting information), the full notation includes the '+' sign and underlining which have the same meaning as in this example.

In the next example on a 4H polytype (Fig. 12), it would have one octahedron per layer and four layers. The connectivity from the first to the second layer would be a pair of face-shared octahedra, then from the second layer to the third layer would be three-corner-shared octahedra, and this pattern is also repeated from the third to the fourth layer. Finally, the terminal fourth layer would once again have three-corner-shared octahedra. Hence, a 4H polytype would have a reduced notation of 1-4(CCC)F(CCC)F or the full notation 1-4 (¹C₃₄₆ ¹C₃₄₆ ¹C₃₄₆) ¹²⁵F_{3,4,6} (¹C₃₄₆ ¹C₃₄₆ ¹C₃₄₆) ¹²⁵F_{3,4,6}. Since all three shared corners are equivalent, there is no need to underline any section of this notation.

Similarly, it can also be seen that when this terminology is used in a multilayered 1D nanotube, as in (HMTA)₃PbBr₇, it also becomes highly awkward. In (HMTA)₃PbBr₇, there are six octahedra in one layer and the octahedra are face shared to give three face-shared dimers per layer. The repeating unit has two layers and the two layers are related by a 6_1 screw axis and connected at the edge to form a rugged ring. Since the cyclic connectivity forms only across two layers, the square parenthesis is employed across the first and second sections. Lastly, the repeating unit connects to the next repeating unit through a 6_1 -screw axis, all of which are corner shared. Furthermore, in the full notation, we also have to account for the effect of the pair of octahedra connecting from the bottom layer to the higher layer and *vice versa* and, thus, an additional '+' and '-' sign is added to account for such an effect. Thus, (HMTA)₃PbBr₇ would have the reduced notation Cyclo[3(2-F)-2(6₁CCCCCCC)]₆₁CCCCC and the full notation would be cyclo[3(2 ^XF₃₄₆ ¹²⁵F_X)-2(6₁ ⁶⁺C₁ ³⁻C₅ ⁶⁺C₁ ³⁻C₅ ⁶⁺C₁ ³⁻C₅)] (6₁ ⁶⁺C₁ ³⁻C₅ ⁶⁺C₁ ³⁻C₅ ⁶⁺C₁ ³⁻C₅). It can be seen from the three listed examples that such a notation would not only be awkward and long, but also confusing. Hence, when applic-

Figure 12

The structure shown here has one octahedron per layer and the repeating unit has four layers. The first and second layers are connected through face sharing, while the second layer is connected to the third layer through three corner-sharing connections. The third and fourth layers are connected through face sharing and the repeating unit is connected to the next repeating unit through three corner-sharing connections. Therefore, the 4H polytype would take the reduced notation 1-4(CCC)F(CCC)F. In the full notation this structure would be written as 1-4 (¹C₃₄₆ ¹C₃₄₆ ¹C₃₄₆) ¹²⁵F_{3,4,6} (¹C₃₄₆ ¹C₃₄₆ ¹C₃₄₆) ¹²⁵F_{3,4,6}. The structure illustrated here is taken from θ -ACASnI₃ (Stoumpos *et al.*, 2017).

able, the existing Gard and Ramsdell notations should be utilized or, in such multilayered tubular structures, be avoided altogether.

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References

- Ali, B. F., Al-Far, R. & Haddad, S. (2007). *Acta Cryst.* **E63**, m1569.
- Arora, Y., Seth, C. & Khushalani, D. (2019). *Langmuir*, **35**, 9101–9114.
- Billing, D. G. & Lemmerer, A. (2006). *Acta Cryst.* **C62**, m174–m176.
- Febriansyah, B., Neo, C. S. D., Giovanni, D., Srivastava, S., Lekina, Y., Koh, T. M., Li, Y., Shen, Z. X., Asta, M., Sum, T. C., Mathews, N. & England, J. (2020). *Chem. Mater.* **32**, 4431–4441.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Guinier, A., Bokij, G. B., Boll-Dornberger, K., Cowley, J. M., Āurovič, S., Jagodzinski, H., Krishna, P., de Wolff, P. M., Zvyagin, B. B., Cox, D. E., Goodman, P., Hahn, Th., Kuchitsu, K. & Abrahams, S. C. (1984). *Acta Cryst.* **A40**, 399–404.
- Hamdi, B., Zouari, R. & Ben Salah, A. (2018). *Superlattice Microstruct.* **123**, 97–110.
- Hartono, N. T. P., Sun, S., Gélvez-Rueda, M. C., Pierone, P. J., Erodici, M. P., Yoo, J., Wei, F., Bawendi, M., Grozema, F. C., Sher, M., Buonassisi, T. & Correa-Baena, J. (2019). *J. Mater. Chem. A*, **7**, 23949–23957.
- Jodlowski, A. D., Yépez, A., Luque, R., Camacho, L. & de Miguel, G. (2016). *Angew. Chem. Int. Ed.* **55**, 14972–14977.
- Jung, M.-H. (2020). *New J. Chem.* **44**, 171–180.
- Li, X., He, Y., Kepenekian, M., Guo, P., Ke, W., Even, J., Katan, C., Stoumpos, C. C., Schaller, R. D. & Kanatzidis, M. G. (2020). *J. Am. Chem. Soc.* **142**, 6625–6637.
- Lin, H., Zhou, C., Tian, Y., Besara, T., Neu, J., Siegrist, T., Zhou, Y., Bullock, J., Schanze, K. S., Ming, W., Du, M.-H. & Ma, B. (2017). *Chem. Sci.* **8**, 8400–8404.
- Liu, G., Liu, J., Tao, X., Li, D. & Zhang, Q. (2016). *Inorg. Chem. Front.* **3**, 1388–1392.
- Liu, Y., Liu, D. & Wu, T. (2019). *J. Solid State Chem.* **269**, 220–224.
- Pan, J., Sun, A.-H., Han, S.-D., Wei, L., Li, J.-H. & Wang, G.-M. (2017). *J. Clust. Sci.* **28**, 2669–2679.
- Ramsdell, L. S. (1947). *Am. Mineral.* **42**, 64.
- Seth, C., Jana, D., Jindal, V., Khushalani, D. & Ghosh, S. (2019). *J. Phys. Chem. C*, **123**, 16449–16455.
- Skelton, B. W., Kokozay, V. N., Vassilyeva, O. Y. & Buvaylo, E. A. (2019). CSD Communication.
- Soe, C. M. M., Stoumpos, C. C., Kepenekian, M., Traoré, B., Tsai, H., Nie, W., Wang, B., Katan, C., Seshadri, R., Mohite, A. D., Even, J., Marks, T. J. & Kanatzidis, M. G. (2017). *J. Am. Chem. Soc.* **139**, 16297–16309.
- Stoumpos, C. C., Mao, L., Malliakas, C. D. & Kanatzidis, M. G. (2017). *Inorg. Chem.* **56**, 56–73.
- Yuan, Z., Zhou, C., Tian, Y., Shu, Y., Messier, J., Wang, J. C., van de Burgt, L. J., Kountouriotis, K., Xin, Y., Holt, E., Schanze, K., Clark, R., Siegrist, T. & Ma, B. (2017). *Nat. Commun.* **8**, 14051.