An extended Tolerance Factor approach for organic–inorganic perovskites†

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Goldschmidt’s concept of ionic Tolerance Factors was recently shown to be a valuable guideline for the preparation of new compounds within the field of organic–inorganic perovskites. Here, we extend this approach and calculate Tolerance Factors for over 2500 amine–metal–anion permutations of the periodic table. The results suggest the potential existence of more than 600 undiscovered hybrid perovskites including alkaline earth metal and lanthanide based materials.

The large family of solid state perovskites with general formula ABX₃ covers a wide range of fascinating properties, which include both application-oriented phenomena and fundamental physics and chemistry.¹ One of the key aspects that make perovskites so successful is the adaptability of this structure type towards A, B or X site substitution, which allows for tailoring of properties to meet particular requirements.²

During recent years a structurally related family, today known as organic–inorganic hybrid perovskites, has attracted a great deal of attention.³,⁴ In this relatively young family the perovskite architecture is essentially maintained, while at least one ion – usually A or X – is substituted by an organic ion which makes the perovskite a hybrid. Today, research in this emerging field is largely driven by the intriguing properties of the hybrid perovskite [CH₃NH₃]PbI₃ in thin film solar cell devices.⁵,⁶ However, other hybrid perovskites, e.g. the family of perovskite-like metal formates AB(HCOO)₃ (A = protonated amine, B = divalent metal),⁷,⁸ also show interesting properties such as multiferroic⁹ behaviour and tunable mechanical properties.¹⁰,¹¹

Recently, Goldschmidt’s Tolerance Factor (TF) concept, which has been a central mantra in the development of solid state perovskites for decades, was extended to the emerging field of organic–inorganic perovskites.¹² Similar to Goldschmidt’s initial approach,¹³ TFs of hybrid perovskites can be obtained by treating all ions as hard spheres or cylinders in the given crystallographic data, a semi-empirical approach leads to a consistent set of effective ionic radii for organic ions.¹² The concept of describing protonated amines in a perovskite structure as hard spheres is supported by microwave,¹⁴ NMR and diffraction studies, as well as theoretical work. This reveals the highly dynamical nature of protonated amines within the perovskite cavity.¹⁵–¹⁸ Following this concept, TFs of lead halide, divalent metal formate, and tetrahydroborate based perovskites have been calculated and very good agreement between experimental observations and theory was found.¹²,¹⁹,²⁰ For example, the TF concept has been successfully used as a guide in the synthesis of complex hydride perovskite-type materials, including the system [CH₃NH₃]Ca(BH₄)₂.²¹ According to the current state of knowledge, hybrid perovskites are expected to form for TFs between 0.8 and 1, as in the case of solid state perovskites. This finding also includes hybrid formates with an anti-anti formate connectivity; however, for syn-anti bridged formates, the size of the ReO₃-like cavity is reduced and even TFs below 0.8 lead to a perovskite-like architecture.²²

The TF concept can also help to explain the existence of low-dimensional materials with perovskite-like building motifs. The sole usage of amines that do not fit into the ReO₃ cavity (TFs > 1) leads to low dimensional compounds, e.g. [NC₄H₈]CdCl₄, [C₇H₇]-PbI₃ and [(CH₃)₂NH]PbI₃.²³–²⁴ In such compounds 1D chains of face-sharing octahedra are separated by protonated amines. A change in stoichiometry consequently leads to a different class of 2D materials such as [C₄H₄NH₂]₃CuCl₄₃, [CH₃NH₃]FeCl₄ and [C₄H₄NH₃]₂MnCl₄ where single layers of corner sharing MX₆-octahedra are separated by large protonated amines. The partial substitution of the large amine with a smaller amine then leads to compounds such as ((C₄H₄NH₂)₂(CH₃NH₃)SN₃I₃ and (NH₂CNH₂)₂(CH₃NH₃)2Sn₄I₈.²⁶ In these Ruddlesden–Popper type phases, perovskite-layers with TFs between 0.8 and 1.0 containing the smaller amine are separated by larger protonated amines that do not fit into the ReO₃-like cavity.⁴

Motivated by the latest developments in this fast moving field, we have calculated Tolerance Factors for a wide range of possible amine–metal–anion permutations in the periodic table.
and shown that a vast number of hybrid perovskites remain to be discovered.

**Approach and discussion**

Similar to Goldschmidt’s initial approach, (effective) ionic radii are used for calculating Tolerance Factors of hybrid perovskites. Protonated amines are treated as spheres with an effective radius \( r_{A,ff} \), and organic ions as cylinders with effective height \( h_{X,ff} \) and effective radius \( r_{X,ff} \) of the cylinder, respectively. A detailed description of how to obtain effective ionic radii of organic ions is given in ref. 12. TFs of hybrid perovskites were calculated according to Goldschmidt’s equation,

\[
\text{TF} = \left( \frac{r_{A,ff} + r_{X,ff}}{2h_{X,ff}} \right)^{0.5} + \left( \frac{r_{A,eff} + r_{X,eff}}{2h_{X,eff}} \right)^{0.5}
\]

with TF being the Tolerance Factor, \( r_{A,eff} \), the effective ionic radius of the protonated amine \( A \), \( r_{X,eff} \) the ionic radius of the anion \( X \), and \( r_{A} \) the ionic radius of the divalent metal ion \( B \) in a perovskite with the general formula \( ABX_3 \). TFs of the hybrids with molecular (organic) anions were calculated using the modified Goldschmidt’s equation

\[
\text{TF} = \left( \frac{r_{A,ff} + r_{X,ef}}{2h_{X,eff}} \right)^{0.5} + \left( \frac{r_{A,eff} + r_{X,eff}}{2h_{X,eff}} \right)^{0.5}
\]

The effective radii and heights of molecular anions were calculated according to our previous publication. The ionic radii from Shannon were used which was calculated by using an ionic radius of 177 pm for C.

For \([\text{C}_7\text{H}_7]^+ \) (tropylium), a radius of 333 pm was used which was calculated by using an ionic radius of 177 pm for \( \text{C}_7\text{H}_7^+ \). (A-CdI_3) leads to a larger ReO_3-like cavity so that amines with larger \( \text{Cd} \), \( \text{CdI}_2 \), \( \text{CdI}_3 \) and \( \text{CdI}_4 \) (anti formate) \( \text{CdI}_4 \) (anti connectivity of the formate).

A divalent metal cation was selected according to the stability of the divalent oxidation state in coordination compounds. The effective radii of the protonated amines \([\text{NH}_4]^+ \) (ammonium, 146 pm), \([\text{NH}_3\text{OH}]^+ \) (hydroxylammonium, 216 pm), \([\text{CH}_2\text{NH}_3]^+ \) (methylammonium, 217 pm), \([\text{NH}_2\text{NH}_2]^+ \) (hydrazinium, 217 pm), \([\text{CH}_3\text{NH}_3]^+ \) (azetidinium, 250 pm), \([\text{CH}^+\text{NH}_3]^+ \) (formamidinium, 253 pm), \([\text{C}_3\text{N}_2\text{H}_5]^+ \) (imidazolium, 258 pm), \([\text{CH}_2\text{CH}_2\text{NH}_3]^+ \) (dimethylammonium, 272 pm), \([\text{CH}_3\text{CH}_2\text{NH}_3]^+ \) (ethylammonium, 274 pm), \([\text{NH}_4]^+ \) (guanidinium, 278 pm) and \([\text{CH}_3]\) \( \text{N}^+ \) (tetramethylammonium, 292 pm) were used from ref. 12. The effective radii of \([\text{C}_3\text{H}_4\text{NS}]^+ \) (thiazolium, 320 pm) and \([\text{NC}_3\text{H}_4]^+ \) (3-pyrollinium, 272 pm) were obtained following the procedure described in previous work. For \([\text{C}_2\text{H}_3]^+ \) (tropylium), a radius of 333 pm was used which was calculated by using an ionic radius of 177 pm for \( \text{C}_2\text{H}_3^+ \). Following our recent publication, the errors of obtained Tolerance Factors are estimated at round 6%. An overview of the applied procedure and the ions used is given in Fig. 1.

The permutations of 13 different protonated amines, 8 different anionic species and 21 divalent metal ions lead to 2352 TFs. A full list of all calculated TFs is given in the ESI (Table S1-1†). Out of 2352 calculated TFs, 742 show TFs between 0.8 and 1.0 that include approximately 140 known materials, such as the well-characterized hybrid perovskites \([\text{CH}_3\text{NH}_3]^+ \text{PbI}_3 \) (TF = 0.912), \([\text{CH}_3\text{NH}_3]^+ \text{SnI}_4 \) (TF = 0.922), \([\text{CH}_2\text{NH}_3]^+ \text{EuI}_4 \) (TF = 0.917), the series of \([\text{AmH}]\) \( \text{M} \) (HCOO)_3 \) (4-12, 6-1 topology and anti-anti formate bridges) and \([\text{AmH}]\) \( \text{M} \) (N), and metastable compounds, \([\text{NH}_4]^+ \text{CaCl}_3 \) (TF = 0.823). To the best of our knowledge, only a few formate based compounds are known where TFs considerations lead to wrong conclusions, although preliminary DFT results suggest the existence of polymorphism in some of these frameworks. e.g. \([\text{NH}_3\text{NH}_2]^+ \text{Mg(HCOO)}_3 \) (TF = 0.845, a 4-6, 6 metal-formate framework with chiral hexagonal channels). The TF considerations discussed above predict around 600 hypothetical organic–inorganic perovskites that have not yet been reported. Clearly, it is not expected that all of the 600 hypothetical compounds can be made, nor that they will be stable under ambient conditions, but the experience to date with TFs points to the likelihood that many of these compounds will indeed be discovered. The strength of this semi-empirical approach in comparison with more accurate, modern computational techniques lies in its simplicity, making it a powerful and rapid tool for experimental scientists.

The influence of the size and anisotropy of the linking anion on the TFs is highlighted in Fig. 2 for iodides and formates, while the S.I. contain plots for all other halides, cyanides, azides and borohydrides. Comparing iodides (\( r_e = 220 \text{ pm} \)) and anti-anti formates (\( r_{A,eff} = 136 \text{ pm} \), \( h_{X,eff} = 447 \text{ pm} \)), the anisotropy of the organic formate together with its smaller \( r_{X,eff} \) leads to a larger ReO_3-like cavity so that amines with larger effective radii can be incorporated into the framework. At the same time, the incorporation of small protonated amines would lead to a reduced packing density (TF < 0.8). Consequently, for a fixed divalent metal the size-range of protonated amines that fit in the cavity is shifted to higher values. For example, for \( B = \text{Cd}^{2+} \) (\( r_b = 95 \text{ pm} \)), TFs between 0.8 and 1.0 can be found for \( r_{X,eff} \) (A-CdI_3) = 146–217 pm and \( r_{X,eff} \) (A-Cd(HCOO)_3) = 250–292 pm (anti-anti connectivity of the formate).

Today, promising synthetic approaches towards hybrid perovskite frameworks include solid–solid diffusion-based reactions and solution chemistry methods. For example, a simple diffusion based solid-state reaction at 100–200 °C can be used for the preparation of \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) and \( \text{CH}_3\text{NH}_3\text{EuI}_4 \) starting from \( \text{MI}_2 \) (\( M = \text{Pb}^{2+} \), \( \text{Eu}^{3+} \)) and \( \text{CH}_3\text{NH}_3\text{I} \). This reaction scheme looks very comprehensive for the preparation of halide-based hybrids and could potentially be applied to most of the metal cations considered in this work. However, not all protonated amines, e.g. azetidinium, hydrazinium and hydroxylammonium, are stable at the required temperatures.
and new synthetic procedures must be developed. For molecular
anion based hybrids, solution chemistry approaches provide a powerful method in many cases.\textsuperscript{34,35}

The wide applicability of TFs for hybrid perovskites suggests
that the packing density is a crucial factor for the formation of a
3D hybrid perovskite framework. Within hybrid frameworks,
the complexity of the bonding allows for tuning different
properties over a wide range, e.g., band-gap engineering due to B
or X site substitution in halide based compounds or altering
magnetic properties in azido-bridged frameworks.\textsuperscript{34–36} Hydrogen
bonding interactions between the protonated amine and the
cavity have been shown to have a large impact on the materials’
properties.\textsuperscript{45} For instance, in iodide and formate based
frameworks, bonding interactions between amines and the
frameworks influence the mechanical properties and are responsible
for temperature-driven order–disorder transitions.\textsuperscript{37–39,47}

In conclusion we calculated Tolerance Factors for over
2300 hypothetical amine–metal–anion permutations based on
halides and molecular (organic) anions such as (HCOO)\textsuperscript{−} , (CN)\textsuperscript{−}
and (N\textsubscript{3})\textsuperscript{−} . Of these, 742 show TFs between 0.8 and 1 are pre-
dicted to adopt the perovskite structure. To our knowledge, the
group of 742 compounds includes about 140 known examples

and more than 600 unknown hypothetical compounds. Interest-
ingly, the doping of [CH\textsubscript{3}NH\textsubscript{3}]PbI\textsubscript{3} on the lead site with Ca\textsuperscript{2+},
Se\textsuperscript{2+} and Cd\textsuperscript{2+} was recently reported and is encouraging for further research.\textsuperscript{48} However, most of the predicted compounds
herein, e.g. [CH\textsubscript{3}NH\textsubscript{3}]SrI\textsubscript{3} and [CH\textsubscript{3}NH\textsubscript{3}]CaI\textsubscript{3}, are not expected to
be good electrical conductors. More likely, related to their
hybrid nature, they may show ferroelectric and ferroelastic
properties which are of great importance for switching devices
and sensor applications. In this context, alkaline earth and first
row transition metal based hybrids are of particular interest due
to their high abundance.\textsuperscript{49} Other compounds, such as lanthan-
ide based hybrids, are expected to show interesting optical
properties. Together with the large tuning adaptability of the
perovskite structure, we expect that the family of hybrid
perovskites will have a prominent influence on materials
science in the future.

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References


2. (a) D. Neagu, G. Tsekouras, D. N. Miller, H. Ménard and
J. T. S. Irvine, Nat. Chem., 2013, 5, 916–923; (b) P. Davies,
H. Wu, A. Borisievich, I. Molodetsky and L. Farber, Annu.
Rev. Mater. Res., 2008, 38, 369–401; (c) N. Zhang, H. Yokota,
A. M. Glazer, Z. Ren, D. A. Keen, D. S. Keeble, P. A. Thomas
and Z.-G. Ye, Nat. Commun., 2014, 5, 5231; (d) Y. Kobayashi,
M. Tian, M. Eguchi and T. E. Mallouk, J. Am.


Chem. Soc., 2009, 131, 6050–6051; (b) M. Liu,

7. Z. Wang, B. Zhang, T. Otsuka, K. Inoue, H. Kobayashi and

2010, 22, 1526–1533; (b) R. Shang, S. Chen, K.-L. Hu,
Z.-C. Jiang, B.-W. Wang, M. Kurmoo, Z.-M. Wang and

9. (a) M. Sánchez-Andújar, L. C. Gómez-Aguirre, B. Pato
Doldán, S. Yáñez-Vilar, R. Artiaga, A. L. Llamas-Saiz,
R. S. Manna, F. Schnelle, M. Lang, F. Ritter,
A. A. Haghighirad and M. A. Seharis-Rodriguez,
CrystEngComm, 2014, 16, 3558; (b) P. Jain,
V. Ramachandran, R. J. Clark, H. D. Zhou, B. H. Toby,


13 V. M. Goldschmidt, Naturwissenschaften, 1926, 14, 477–485.


