The scarcity of nitrogen in Earth’s crust, combined with challenging synthesis, have made inorganic nitrides a relatively-unexplored class of compounds compared to their naturally-abundant oxide counterparts. To facilitate exploration of their compositional space via a priori modeling, and to help a posteriori structure verification not limited to inferring the oxidation state of redox-active cations, we derive a suite of bond-valence parameters and Lewis-acid strength values for 76 cations observed bonding to N\textsubscript{3}-, and further outline a baseline statistical knowledge of bond lengths for these compounds. We examine structural and electronic effects responsible for the functional properties and anomalous bonding behavior of inorganic nitrides, and identify promising venues for exploring uncharted compositional spaces beyond the reach of high-throughput computational methods. We find that many mechanisms of bond-length variation ubiquitous to oxide and oxysalt compounds (e.g., lone-pair stereoactivity, the Jahn-Teller and pseudo Jahn-Teller effects) are similarly pervasive in inorganic nitrides, and are occasionally observed to result in greater distortion magnitude than their oxide counterparts. We identify inorganic nitrides with multiply-bonded metal ions as a promising venue in heterogeneous catalysis, e.g. in the development of a post-Haber-Bosch process proceeding at milder reaction conditions, thus representing further opportunity in the thriving exploration of the functional properties of this emerging class of materials.
On the crystal chemistry of inorganic nitrides: Crystal-chemical parameters and opportunities in the exploration of their compositional space

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ABSTRACT: The scarcity of nitrogen in Earth’s crust, combined with challenging synthesis, have made inorganic nitrides a relatively-unexplored class of compounds compared to their naturally-abundant oxide counterparts. To facilitate exploration of their compositional space via a priori modeling, and to help a posteriori structure verification not limited to inferring the oxidation state of redox-active cations, we derive a suite of bond-valence parameters and Lewis-acid strength values for 76 cations observed bonding to N\(^3\), and further outline a baseline statistical knowledge of bond lengths for these compounds. We examine structural and electronic effects responsible for the functional properties and anomalous bonding behavior of inorganic nitrides, and identify promising venues for exploring uncharted compositional spaces beyond the reach of high-throughput computational methods. We find that many mechanisms of bond-length variation ubiquitous to oxide and oxysalt compounds (e.g., lone-pair stereactivity, the Jahn-Teller and pseudo Jahn-Teller effects) are similarly pervasive in inorganic nitrides, and are occasionally observed to result in greater distortion magnitude than their oxide counterparts. We identify inorganic nitrides with multiply-bonded metal ions as a promising venue in heterogeneous catalysis, e.g. in the development of a post-Haber-Bosch process proceeding at milder reaction conditions, thus representing further opportunity in the thriving exploration of the functional properties of this emerging class of materials.

Introduction

The predominance and variety of oxide and oxysalt compounds as minerals in Earth’s crust means that they were inevitably among the first materials to be methodically characterized and examined for interesting properties, occupying scientists for decades in trying to decipher, reproduce, and enhance their behavior. Conversely, inorganic nitrides, here defined as ionic/covalent compounds with N\(^3\) as the main anion, are a relatively-unexplored class of compounds owing to (1) the scarcity of nitrogen minerals in Earth’s crust due to various biological and geological transport processes drawing nitrogen away from the crust\(^1\) (not limited to their reaction with water to form hydroxides and ammonia\(^2\)), and (2) challenging synthesis.\(^3\)

Systematic investigation of nitrides began in the late 1930s with the work of Juzar and collaborators who mainly focused on lithium compounds for their relative ease of preparation.\(^4-6\) Rapid progression in the synthesis and characterization of nitride compounds followed the introduction of several new methods of preparation in the 1980s. This sudden burst of interest eventually led to the successful synthesis of many compounds suited to single-crystal X-ray diffraction, resulting in collection of significantly more accurate bond lengths compared to those determined via powder diffraction.\(^7\) Several reviews on the descriptive crystal chemistry of inorganic nitrides followed\(^8-14\) (more recent reviews include those of Höhn & Niewa for non-main group elements,\(^15\) and Tareen et al. for mixed ternary transition metal nitrides\(^16\)), and the chemistry of nitrides was soon likened to that of silicates;\(^10\) the term nitridometalate was introduced to describe compounds containing covalent complex anions [M\(_n\)N\(_x\)]\(^y\) (in relation to oxometallates, commonly called oxyanions in the Earth sciences),\(^11,12\) reflecting the richness of chemistries to come. New classes of inorganic nitrides that were initially considered to be scientific curiosities have since been described as functionally-diverse groups of materials, not limited to the nitridosilicates,\(^6,17\) oxynitrididosilicates,\(^18\) and perovskite-related oxynitrides.\(^19,20\)

Nitrides provide a great opportunity for materials discovery owing to their unique electronic and bonding characteristics. Large-scale computational\(^13,21\) and synthetic efforts (notably by the groups of Francis DiSalvo, Rainer Niewa, Wolfgang Schnick, and Duncan Gregory) to explore their compositional space are underway. These compounds are being investigated for energy conversion and storage,\(^22\) solar-driven CO\(_2\) reduction in Z-scheme-inspired photoelectrochemical cells,\(^23\) as alternatives to metals, metal oxides and metal sulfides in heterogeneous catalysis,\(^24\) in quantum information processing,\(^25\) as piezoelectric\(^26,27\) and photoluminescent\(^28\) materials, electrocatalysts,\(^8,29,30\) electrochemical sensors,\(^31\) photocatalysts,\(^32,33\) photovoltaics,\(^34-36\) photodetectors,\(^37,38\) light-emitting diodes,\(^39,40\) thermoelectrics,\(^26,41\) superconductors,\(^42-44\) as hard coating\(^45\) and ultrahard materials\(^46\) (in their pernitride form), etc. With a relatively slow start compared to oxides and oxysalts, it is no surprise that some of the most exciting properties of these materials are
currently being realized, and that much promise lies ahead
in the exploratory synthesis of functional inorganic nitrides.

The present work is premised on a distillation of crystal-
lographic knowledge for inorganic nitrides, with the goal of
facilitating their characterization and design. Such pursuits
have been eased by the bond-valence model for many clas-
ses of inorganic compounds, which is for example used to
screen compounds in pymatgen\textsuperscript{47} and to infer the oxidation
state of redox-sensitive ions\textsuperscript{48} under the umbrella of the Ma-
terials Project.\textsuperscript{49} Most recently, the bond-topological nature
of the bond-valence model was featured in showing how
bond-length variation (thus polyhedral distortion) is an in-
herent predictably quantifiable by-product of chemical
bonding in inorganic solids\textsuperscript{50} (polyhedral distortion having
crucial implications with regard to the functional properties
of various types of materials not limited to ferroelectric-
ity,\textsuperscript{51,52} piezoelectricity,\textsuperscript{51,53} flexoelectricity,\textsuperscript{54} second-order
nonlinear optical behavior;\textsuperscript{51,55} negative thermal expan-
sion,\textsuperscript{56} and photoluminescence\textsuperscript{57,58}). However, the pa-
rameterization of the bond-valence model is largely incomplete
for cations bonded to N\textsuperscript{3}, and the quality of published bond-
valence parameters is not established. In this work, we use
the method of Gagné & Hawthorne\textsuperscript{59} to derive new bond-
valence parameters for nitrides, provide a scale of Lewis
acidity for nitrides, and further outline a baseline statistical
knowledge of bond lengths for cations bonded to N\textsuperscript{3} as a
contribution to our gradual effort toward modernizing
Shannon’s set of ionic radii\textsuperscript{10} (see refs. 50,61-64 for bond-
length statistics of cations bonded to O\textsuperscript{2}; in prep for cations
bonded to S\textsuperscript{2}, Se\textsuperscript{2-} and/or Te\textsuperscript{2-}). Later in this work, we ex-
plor new and interesting venues for the exploratory syn-
thesis of functional inorganic nitrides from a crystal-chemi-
cal perspective.

Dataset

We used the Inorganic Crystal Structure Database (ICSD)
to extract bond-length data for elements bonded to N\textsuperscript{3} as a
function of oxidation state and coordination number. Data
collection criteria are those outlined by Gagné & Haw-
thorne\textsuperscript{61}: (1) publication date ≥ 1975; (2) \( R_I \leq 0.06; \) (3) the
site of interest is fully occupied by the cation; (4) all bonds
involve ions at fully occupied sites; (5) the cation and anion
sites of interest show no positional disorder; (6) crystallographic data were measured at ambient condi-
tions; (7) no data from powder, electron or synchrotron dif-
fraction were included; (8) for H, only neutron-diffraction
data were collected. The procedure used to determine the
coordination polyhedron in ambiguous cases is also that of
Gagné & Hawthorne.\textsuperscript{61}

Following data collection, we examined structures with
questionable bond-lengths and/or mean bond-lengths for
various problems (e.g. positional/substitutional disorder,
consistent (an)isotropic displacement parameters, high
standard deviations on bond lengths, etc.) and discarded
data which could not be confidentely confirmed.

Mixed-anion coordination polyhedra

Although bond-valence parameters have historically
been derived using cation coordination polyhedra with only
one kind of anion (e.g. BN\textsubscript{3}), it is possible to derive bond-
valence parameters using mixed-anion coordination poly-
hedra, provided that (1) reliable bond-valence parameters
are available for the cation-anion pair(s) that does not enter
the refinement, and (2) each crystallographically-distinct
anion site is fully occupied by a single anion. For example,
one may use bond lengths from a BON\textsubscript{2} coordination poly-
hedron\textsuperscript{62} to refine B-N bond-valence parameters, treating
the B-O bond-valence as a constant calculated using the pa-
rameters of Gagné & Hawthorne.\textsuperscript{59} Due to a general paucity
of data for nitride compounds relative to oxides and oxy-
salts, data for coordination polyhedra containing both O\textsuperscript{2-}
and N\textsuperscript{3-} were also collected. Below, we show for the first
time that the use of mixed-anion coordination polyhedra
leads to the same bond-valence parameters as those
derived with one type of anion, thus allowing the derivation of
bond-valence parameters for cations with otherwise no

data.

The final dataset used to derive the bond-valence param-
eters given in Table 1 consists of 6,770 bond lengths hand-
picked from 1436 coordination polyhedra from 720 crystal-
structure refinements, covering 76 cations bonded to N\textsuperscript{3-}
(and possibly also O\textsuperscript{2-}). The dataset that omits oxygen data
accounts for 4,048 bond lengths taken from 875 cation co-
ordination polyhedra; these data and their basic statistics
are reported in Table 2 and will be discussed further below.

| Ion      | No. of coordination polyhedra | Average observed coordination number | \( S_a (\text{v.u.}) \) | Std. dev. on \( S_a \) | \( R_o (\text{Å}) \) | \( B (\text{Å}) \) | RMSD (v.u.) | Method of derivation (1-CN) |
|----------|-------------------------------|--------------------------------------|------------------------|-------------------------|-----------------|-----------------|----------------|--------------------------------|
| *H*      | 30                            | 3.63 (6)                             | 0.275 (4)              | 0.070                   | 1.713           | 0.312           | 0.111         |                                |
| Li\textsuperscript{+} | 83                            | 3.36 (2)                             | 0.57 (3)               | 0.08                    | 1.537           | 0.301           | 0             |                                |
| Be\textsuperscript{2+} | 51                            | 2.43 (6)                             | 1.24 (3)               | 0.33                    | 1.467           | 0.321           | 0.079         |                                |
| B\textsuperscript{3+}  | 270                           | 2.76 (2)                             | 1.45 (1)               | 0.22                    | 1.401           | 0.261           | 0.094         |                                |
| N\textsuperscript{5+}  | 6                             | 2                                    | 2.5                    |                         | 1.51            | 0.345           | 0.027         |                                |
| Na\textsuperscript{+}  | 74                            | 5.29 (6)                             | 0.189 (2)              | 0.027                   | 1.62            | 0.546           | 0.098         |                                |
| Mg\textsuperscript{2+} | 7                             | 4                                    | 0.5                    |                         | 1.83            | 0.37            | 0.252         |                                |
| Element | Charge | Z | Ionization Energy (eV) | Atomic Radius (Å) | Electronegativity | Density (g/cm³) |
|---------|--------|---|-----------------------|-------------------|------------------|-----------------|
| Al³⁺   | 11     | 13 | 4.20 (9)              | 0.71 (2)          | 1.772            | 0.413           | 0.187           |
| Si⁴⁺   | 14     | 14 | 4.02 (1)              | 0.995 (2)         | 1.742            | 0.422           | 0.175           |
| P⁵⁺    | 15     | 15 | 1.25                  | 1.72              | 0.414            | 0.307           |
| S⁶⁺    | 16     | 16 | 2                     | 1.781             | 0.328            | 0.081           |
| Se⁶⁺   | 18     | 18 | 46                    | 1.731             | 0.366            | 0.075           |
| K⁺     | 19     | 19 | 67                    | 4.64 (9)          | 0.082            | 1.892           | 0.543           | 0.122           |
| Ca²⁺   | 20     | 20 | 5.13 (7)              | 0.90 (5)          | 2.114            | 0.435           | 0.214           |
| V³⁺    | 6      | 6  | 1/3                   | 1.779             | 0.405            | 0.1           |
| V⁵⁺    | 1      | 2  | 1.25                  | 1.93              | 0.399            | 0.2           |
| Cr³⁺   | 26     | 26 | 5.8 (1)               | 0.522 (9)         | 1.796            | 0.403           | 0.611           |
| Cr⁵⁺   | 1      | 4  | 1.25                  | 1.844             | 0.399            | 0.2           |
| Mn²⁺   | 25     | 25 | 5.3 (1)               | 0.377 (9)         | 1.874            | 0.328           | 0.141           |
| Mn⁵⁺   | 3      | 3  | 1                     | 1.759             | 0.399            | 0.124           | 2              |
| Fe²⁺   | 1      | 4  | 1.5                   | 1.924             | 0.399            | 0.075           | 2              |
| Fe⁵⁺   | 3      | 3  | 0.69 (6)              | 1.74              | 0.687            | 0.059           |
| Co⁺    | 1      | 2  | 0.5                   | 1.472             | 0.399            | 0.2           |
| Co²⁺   | 9      | 9  | 0.429 (1)             | 1.626             | 0.485            | 0.049           |
| Co³⁺   | 66     | 66 | 0.5                   | 1.686             | 0.399            | 0.062           | 2              |
| Ni²⁺   | 19     | 19 | 0.44 (1)              | 1.611             | 0.457            | 0.054           |
| Cu⁺    | 9      | 9  | 0.45 (3)              | 1.539             | 0.399            | 0.2           |
| Cu²⁺   | 17     | 17 | 0.36 (1)              | 1.577             | 0.515            | 0.129           |
| Zn²⁺   | 29     | 29 | 0.51 (1)              | 1.792             | 0.292            | 0.264           |
| Ga³⁺   | 4      | 4  | 0.67 (3)              | 1.858             | 0.318            | 0.164           |
| Ge⁴⁺   | 2      | 2  |                       | 1.891             | 0.423            | 0.014           | 3              |
| Se⁶⁺   | 2      | 2  |                       | 1.945             | 0.422            | 0.067           | 3              |
| Rb⁺    | 29     | 29 | 0.130 (2)             | 0.023             | 1.914            | 0.639           | 0.039           |
| Sr²⁺   | 32     | 32 | 0.35 (1)              | 0.12              | 2.269            | 0.441           | 0.215           |
| Y³⁺    | 5      | 5  | 0.5                   | 2.114             | 0.399            | 0.055           | 2              |
| Nb⁵⁺   | 12     | 12 | 1.15 (3)              | 2.052             | 0.404            | 0.057           |
| Mo⁶⁺   | 23     | 23 | 1.5                   | 1.97              | 0.265            | 0.129           |
| Ru⁷⁺   | 49     | 49 | 0.5                   | 1.816             | 0.399            | 0.02           |
| Rh⁷⁺   | 57     | 57 | 0.5                   | 1.795             | 0.399            | 0.023           | 2              |
| Pd⁷⁺   | 59     | 59 | 0.5                   | 1.767             | 0.399            | 0.033           | 2              |
| Ag⁺    | 108    | 108| 0.41 (2)              | 0.12              | 1.926            | 0.277           | 0.089           |
| Cd²⁺   | 54     | 54 | 0.5                   | 1.889             | 0.399            | 0.048           | 2              |
| Sn²⁺   | 51     | 51 | 2/3                   | 1.965             | 0.438            | 0.2           |
| Sn⁴⁺   | 50     | 50 | 2/3                   | 2                 | 0.438            | 0.003           | 2              |
| Cs⁺    | 80     | 80| 9.5 (1)               | 0.106 (1)         | 1.979            | 0.67           | 0.077           |
| Ba²⁺   | 56     | 56 | 0.299 (4)             | 0.067             | 2.432            | 0.405           | 0.171           |
| La³⁺   | 57     | 57 | 8.00 (0.08)           | 0.375 (4)         | 2.177            | 0.52           | 0.192           |
| Element | Value | Reference | Valence | RMSD | Weighted RMSD | Notes |
|---------|-------|-----------|---------|------|--------------|-------|
| Ce³⁺   | 11    | 8.40 (8)  | 0.357 (3) | 0.021 | 2.162 | 0.469 | 0.157 | 2 |
| Ce⁴⁺   | 1     | 6        | 2/3     |       | 2.237 | 0.469 | --   | 2 |
| Pr³⁺   | 3     | 7        | 3/7     |       | 2.129 | 0.469 | 0.183 | 2 |
| Nd⁴⁺   | 8     | 6.7 (2)  | 0.45 (1) | 0.06  | 2.051 | 0.555 | 0.256 | |
| Sm³⁺   | 7     | 3/7     |         |       | 2.042 | 0.469 | 0.119 | 2 |
| Eu²⁺   | 5     | 8.4 (4)  | 0.24 (1) | 0.07  | 1.952 | 0.587 | 0.089 | |
| Eu³⁺   | 3     | 6        | 0.5     |       | 2.238 | 0.275 | 0.279 | |
| Gd³⁺   | 2     |          |         |       | 2.064 | 0.38  | 0.017 | |
| Tb³⁺   | 3     |          |         |       | 2.042 | 0.415 | 0.019 | |
| Dy³⁺   | 1     |          |         |       | 1.978 | 0.469 | --   | 2 |
| Ho³⁺   | 2     | 6        | 0.5     |       | 2.097 | 0.391 | 0.25  | 1 |
| Er³⁺   | 4     | 6        | 0.5     |       | 2.057 | 0.498 | 0.138 | |
| Yb³⁺   | 3     | 6.3 (1)  | 0.474 (8) | 0.035 | 1.928 | 0.584 | 0.19  | |
| Lu³⁺   | 1     | 6        | 0.5     |       | 1.966 | 0.487 | --   | 1 |
| Hf⁴⁺   | 1     | 8        | 0.5     |       | 2.023 | 0.399 | --   | 2 |
| Ta⁵⁺   | 5     | 4        | 1.25    |       | 2.047 | 0.399 | 0.038 | 2 |
| W⁶⁺    | 27    | 4        | 1.5     |       | 2.026 | 0.399 | 0.089 | 2 |
| Pt²⁺   | 15    | 4        | 0.5     |       | 1.817 | 0.351 | 0.063 | |
| Au⁺    | 2     | 2        | 0.5     |       | 1.743 | 0.399 | 0.187 | 2 |
| Ti⁺    | 8     | 6.88 (8) | 0.145 (2) | 0.013 | 2.114 | 0.493 | 0.03  | |
| Pb²⁺   | 2     | 6.0 (3)  | 0.33 (2) | 0.06  | 2.058 | 0.529 | 0     | |
| Bi³⁺   | 3     |          |         |       | 2.066 | 0.438 | 0.018 | 2 |
| U⁴⁺    | 1     | 8        | 0.5     |       | 2.129 | 0.422 | --   | 3 |
| U⁶⁺    | 2     |          |         |       | 2.035 | 0.422 | 0.053 | 3 |

Mean RMSD n ≥ 10 0.122
Mean RMSD weighted by number of CP 0.120

*neutron-diffraction data
1: $R_o$ fixed to predicted value
2: $B$ fixed to family average
3: $B$ fixed to 0.399 Å

Data from mixed-anion coordination polyhedra are omitted in the calculation of AOCN and $S_a$; more detail on these data are given in Table 2

**Derivation of bond-valence parameters**

Although the first proposal of a relation between bond length and bond strength can be attributed to Pauling, the first universal two-body correlation between these variables was described by Brown and Shannon in what ultimately developed into the bond-valence model. The bond-valence relation was initially proposed as an inverse power equation and later reformulated to

$$S_i = \exp \left( \frac{R_o - R_i}{B} \right)$$

where $R_i$ is the bond length, $S_i$ is the bond valence, and $R_o$ and $B$ are bond-valence parameters, derived on the basis of ion pair. The valence-sum rule of the bond-valence model is of particular importance as a basis for optimizing bond-valence parameters. The rule states that the sum of the bond valences at each atom is equal to the magnitude of the atomic valence,

$$\sum S_{ij} = \sum_j \exp \left( \frac{R_o - R_{ij}}{B} \right) = V_i$$

where the sum is taken over the $j$ nearest neighbours of cation $i$, and where $V_i$ is the atomic valence (oxidation state) of cation $i$. Following a review of methods used for the derivation of bond-valence parameters, Gagné & Hawthorne proposed the Generalized Reduced Gradient (GRG) method of RMSD minimization for the derivation of new bond-valence parameters (where the RMSD is from the valence-sum rule, in valence units v.u.). This method uses the GRG algorithm to find the global minimum of

$$\text{RMSD} = \sqrt{\frac{\sum_i \left( \sum_j S_{ij} - V_i \right)^2}{n}} \to 0$$

(eq.3)
where the minimization is done over \( n \) observed coordination polyhedra for a given cation-anion pair. Gagné & Hawthorne further propose the use of a weighting scheme that finds a balance between overall fit (RMSD; eq.3) and fit on the basis of cation coordination number

\[
\text{RMSD}_{\text{CN}} = \sqrt{\frac{\sum (\text{CN}_{ij} - \langle \text{CN} \rangle)^2}{\text{n}}} \rightarrow 0 \quad \text{(eq.4)}
\]

where the term between brackets is the mean bond-valence sum on the basis of coordination number, and where the summation is done over \( n \) observed coordination numbers. This added term ensures that a potentially disproportionate amount of data for a given cation coordination number does not take over the optimization procedure, which can otherwise result in faulty bond-valence parameters. We used the 2:1 weighting scheme between RMSD and \( \text{RMSD}_{\text{CN}} \) of Gagné & Hawthorne to derive the bond-valence parameters of Table 1.

**Bond-valence parameters for mixed-anion polyhedra**

Bond-valence parameters were refined with the GRG method for \( \text{Ba}^{2+}, \text{Cr}^{3+} \) and \( \text{Cu}^{2+} \) with and without their mixed-anion (\( N^3 \) and \( O^2 \)) coordination polyhedra to test whether use of mixed-anion coordination polyhedra leads to the same bond-valence parameters as those derived with only one type of anion. For \( \text{Ba}^{2+}, R_o = 2.432 \text{ Å} \) and \( B = 0.405 \text{ Å}, n = 53 \), including 9 coordination polyhedra with one or more oxygen anion. Removing those 9 coordination polyhedra, \( R_o \) and \( B \) refine to 2.433 and 0.406 Å, respectively. For \( \text{Cr}^{3+}, R_o = 1.796 \text{ Å} \) and \( B = 0.403 \text{ Å}, n = 26 \), including 14 coordination polyhedra with one or more oxygen anion. Their removal gives \( R_o = 1.796 \text{ Å} \) and \( B = 0.406 \text{ Å} \). For \( \text{Cu}^{2+}, R_o = 1.577 \text{ Å} \) and \( B = 0.515 \text{ Å}, n = 17 \), including 13 coordination polyhedra with one or more oxygen anion. Their removal gives \( R_o = 1.585 \text{ Å} \) and \( B = 0.490 \text{ Å} \). These results show that using mixed-anion coordination polyhedra for refining new bond-valence parameters is justified, provided that the bond-valence parameters used to convert the concerned bond lengths into constants that do not enter the refinement are known to be of high quality. Thus, mixed-anion coordination polyhedra were used in deriving the new set of cation-\( N^3 \) bond-valence parameters below (Table 1).

**Bond-valence parameters for cations observed in multiple coordination numbers**

To refine both bond-valence parameters \( R_o \) and \( B \) for an ion pair (see equation 1), such ion pair must be observed in at least two different coordination environments, either in terms of cation coordination number, or in terms of mixed-anion ratio. Where this is not observed, either \( R_o \) or \( B \) must be fixed, and the other parameter refined. In our dataset, 45 cations are observed in more than one coordination number. Of those, 37 have enough data (and data of high enough quality) for confident derivation of their bond-valence parameters, and an additional 3 (\( \text{Gd}^{3+}, \text{P}^{5+} \) and \( \text{S}^{6+} \)) have varying mixed-anion ratios that allow refinement of both \( R_o \) and \( B \) despite occurring in only one coordination number. Together, they account for 1168 of the 1436 coordination polyhedra in our final dataset. Bond-valence parameters for these 40 cations were derived optimizing a 2:1 ratio between equations (3) and (4), as described above, and are given in Table 1.

We then plotted the ratio of bond-valence parameter \( R_o \) and the observed mean bond-length for the cations (\( R_{ij} \)) (weighting each coordination number equally, using only coordination polyhedra where the cation is bonded solely to \( N^3 \)) to the \( n \)th ionization energy of the cation, a relation first identified by Gagné & Hawthorne.\(^{59} \) This is shown in Fig. 1, with best-fit equation

\[
\frac{R_o}{\langle R_{ij} \rangle} = 7.28 \times 10^{-3} \sqrt{IE} + 0.526.
\]

Excellent agreement is observed with \( R^2 = 0.86 \), which increases to \( R^2 = 0.92 \) when removing data points for \( \text{Ag}^+ \) and \( \text{Li}^+ \) (Gagné & Hawthorne found \( R^2 = 0.75 \) for \( O^2 \), for 90 cations\(^{59} \)). Thus, the validity of using this relation to extrapolate values of \( R_o \) for cations observed in only one coordination number is confirmed.

**Comparison to \( O^2 \) bond-valence parameters**

For the 40 cations for which both \( R_o \) and \( B \) were refined, the mean increase in \( R_o \) and \( B \) are 0.064 and 0.023 Å, respectively, in comparison to the parameters of Gagné & Hawthorne.\(^{59} \) When weighting these changes by the number of coordination polyhedra used for each ion, these numbers are 0.092 and -0.011 Å, respectively. The largest change is for \( \text{Li}^+ \); for \( O^2, R_o = 1.062, B = 0.642 \text{ Å} \), and for \( N^3, R_o = 1.713, B = 0.312 \text{ Å} \). As discussed above, this variation is an artifact of a shallow RMSD global minimum (typical of alkali and alkaline-earth metals), whereby large changes in the bond-valence parameters lead to only slight changes in RMSD. A lower value of \( R_o \) for \( N^3 \) vs \( O^2 \) is usually associated with an increased value for \( B \), and vice versa.
Bond-valence parameters for cations observed in one coordination number

Bond-valence parameters for the 36 ion pairs observed in only one coordination number, or for which not enough data are available to refine both bond-valence parameters with confidence, were derived in the following way:

1. Fix $R_o$ to the value predicted by equation (5). Let $B$ refine via the GRG method. If the value for $B$ falls within a range similar to that of ions with similar crystal-chemical behavior, accept the bond-valence parameters. Otherwise, move on to (2);

2. Fix $B$ to the family average (e.g. 0.399 Å for the transition metals) or to a value compatible with ions of similar crystal-chemical behavior. Let $R_o$ refine and see if it falls within a reasonable range (typically within a 6.0% difference, the average deviation between observed and predicted values of $R_o$ for the 40 cations for which both $R_o$ and $B$ were refined). If not, move on to (3);

3. Fix $B$ to its mean value for all families combined (0.422 Å) and let $R_o$ refine. This is typically done where there are insufficient data available to make a reasonable estimate of $B$ (e.g. for actinides U$^{4+}$ and U$^{6+}$).

As discussed in Gagné & Hawthorne, fixing the value of $R_o$ is less forgiving than fixing that of $B$ and should be done with caution. For the 36 cations considered here, we fixed $R_o$ for 4 and $B$ for 32 ion pairs (the method of derivation is identified in Table 1).

Anion sum verification

For simplicity, bond-valence parameters are usually derived by optimizing the valence-sum rule for cations (the work of Krivovichev & Brown being a notable exception). However, we emphasize that the valence-sum rule applies equally to cations and anions, and that good agreement for cation bond-valence sums in no way implies good agreement for anion bond-valence sums (and vice versa). It is imperative that new bond-valence parameters be checked against both these quantities, on a large set of crystal structures, before they should be widely accepted. Of the 70+ publications that have given bond-valence parameters since the inception of the model (https://www.iucr.org/__data/assets/file/0007/126574/bvparn2016.cif), such verification has only been done by Krivovichev & Brown for the Pb$^{2+}$-O$^2$ ion pair, by Gagné & Hawthorne for their comprehensive set of bond-valence parameters for cations bonded to O$^2$, and by Siday & Shetty for the P$^{5+}$-S$^2$ ion pair.

We assembled a set of structures with the goal of evaluating as many bond-valence parameters as possible from Table 1 (see Table S1), i.e., unless no structure could be evaluated using solely the bond-valence parameters derived in this work. The RMSD for the anion bond-valence sums (BVS) over the resulting set of 52 crystal structures, covering 135 anion coordination polyhedra, is 0.209 v.u. The simple mean deviation is 0.172 v.u., or 5.7% compared to an ideal BVS of 3 v.u. For comparison, the mean cation RMSD for ion pairs with 10 or more coordination polyhedra is 0.122 v.u. (0.120 v.u. over all ion pairs weighted by their number of coordination polyhedra). This is very similar to the value reported by Gagné & Hawthorne for O$^2$, of 0.126 v.u. for $n \geq 10$, (0.124 for all data weighted by their number of coordination polyhedra). These authors also reported a RMSD of 0.104 v.u. over 511 anion coordination polyhedra of O$^2$ (5.2% compared to an ideal BVS of 2 v.u.).

These numbers allow us to make two observations. First, the RMSD of the anion BVS is slightly larger than that of cations. This result is somewhat expected; aside from not being the subject of the optimization, few structures could be evaluated for anion BVS, and those that could were not necessarily ideally suited to the task (e.g. 0.3 < R; < 0.06). Second, we observe slightly higher RMSD values for both cation and anion BVS for structures of N$^{5+}$ vs O$^2$. This is likely a consequence of sampling a wide range of meta-stable nitride structures, as opposed to thermodynamically-stable minerals which make up a greater fraction of the oxide and oxy-salt data of Gagné & Hawthorne. Meta-stable structures generally entail less-than-perfect mapping of bond-length constraints in three-dimensional space (which can be calculated a priori) under the constraints of symmetry and periodicity, leading to higher variations in mean bond lengths across structure types in comparison to thermodynamically-stable structures.

Comparison with published bond-valence parameters

We compared cation and anion bond-valence sums (BVS) obtained using the parameters of this work and the set of soft bond-valence parameters of Chen & Adams which they adapted to the first coordination shell (but did not evaluate for anion BVS). Fewer bond-valence parameters are given by these authors for nitrides; 25 pairs of bond-valence parameters could be compared.

We evaluated anion BVS for these 25 pairs of bond-valence parameters using the relevant subset of structures (25 crystal structures). The resulting mean anion RMSD is 0.258 v.u. for the parameters of Chen & Adams, and 0.236 v.u. for the parameters given in this work. For cation BVS, the mean cation RMSD over the 25 ion pairs is 0.118 v.u. for the parameters of this work, and 0.219 v.u. using the parameters of Chen & Adams. When weighting by the number of coordination polyhedra, these values are 0.136 and 0.369 v.u., respectively. This comparison confirms our choice for using the method of Gagné & Hawthorne, and demonstrates the need to verify anion bond-valence sums a posteriori.

On deriving bond-valence parameters

We stress that there is no good alternative to ensuring the quality of bond-valence parameters than to verify their performance over a large number of crystal structure refinements.

With the strength of the correlation between the ratio of bond-valence parameter $R_o$ and mean-bond-length as a function of the $n$th ionization energy of the cation (equation 5), it may be tempting to derive bond-valence parameters for ion pairs without empirical data by reversing equation 5, taking the mean-bond-length to be equal to the some of the constituent ionic radii. However, this practice is fraught with uncertainty due to (1) large uncertainty associated with Shannon’s ionic radii (the subject of upcoming work), and (2) the risk involved in fixing bond-valence parameter $R_o$ (even where experimental data are available). It is for
these reasons that we have refrained from predicting bond-valence parameters which cannot be verified via high-quality experimental data. Even where such data are available, one may easily be misled into reporting “high-quality” bond-valence parameters if their quality is not checked against anion bond-valence sum.

**Derivation of Lewis-acid strengths**

Pearson’s concept of hard and soft acids and bases (HSAB)\(^\text{5,7,6}\) may be conveniently transposed and quantified onto the bond-valence scale as

\[
S_a = \frac{V}{N_i} \quad \text{(eq.6)}
\]

where \(S_a\) is the Lewis acid strength of a cation (analogously, \(S_b\) is the Lewis base strength of anions), \(V\) is its the oxidation state, and \(N_i\) is the average observed coordination number (AOCN) of the cation compiled over a large number of crystal structures.\(^\text{7}\) As such, the Lewis acidity of a cation may be interpreted as the mean observed bond-valence of a cation (or cation group) when bonded to a specific anion (or anion group). Furthermore, its standard deviation (calculated from that of the AOCN) may be interpreted as the ability of the cation to adjust to a range of Lewis base strengths via the valence-matching principle. The valence-matching principle states that the most stable structures will form when the Lewis acid strength of the cation closely matches the Lewis base strength of the anion (with island of stability \(0.5 < S_a/S_b < 2\)).\(^\text{6,8,78}\) This argument has notably been used to predict the weakly bonded constituents (interstitial complex) that link strongly bonded oxyanions to form the crystal structures of minerals,\(^\text{79}\) and to explain the distribution of mineral stoichiometries in nature.\(^\text{80,81}\) Foreseeably, the concept of Lewis acidity/basicity may also be used in a priori analysis, e.g. in crystal-structure prediction and materials design.

Gagné & Hawthorne recently published a revision of the Lewis acidity scale for 135 cations bonded to \(\text{O}^{2-}\).\(^\text{82}\) As Lewis-acid strength is dependent upon the base against which it was measured (and vice versa),\(^\text{83}\) we derive a scale of Lewis acidity for 77 cations bonded to \(\text{N}^{3-}\) (Table 1). On average, Lewis acid strength values increase by 0.115 v.u. for cations bonded to \(\text{N}^{3-}\) vs \(\text{O}^{2-}\) (using the scale of Gagné & Hawthorne\(^\text{82}\)), due to generally lower observed cation coordination numbers. Notable discrepancies result from a favored tetrahedral over octahedral coordination for such ions as \(\text{Nb}^{5+}\), \(\text{Mo}^{6+}\), and \(\text{W}^{6+}\) when bonded to \(\text{N}^{3-}\).

**Correlation with ionization energy**

In Fig. 2 we show the correlation between Lewis acid strength and the \(n\)th ionization energy for the 64 cations reported here (\(n < 10\) coordination polyhedra marked by triangles). Linear fit (solid line) to all data gives \(R^2 = 0.83\). For \(n \geq 10\) coordination polyhedra (25 cations), the best-fit equation becomes

\[
S_a = 0.315 IE^{0.807} \quad \text{(eq.7)}
\]

with \(R^2 = 0.91\). Equation (9) is very similar to the equation reported by Gagné & Hawthorne for \(\text{O}^{2-}\) (\(S_o = 0.884 IE^{0.807}, R^2 = 0.90\)).\(^\text{52}\)

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**Figure 2:** Relation between Lewis-acid strength (v.u.) as a function of the \(n\)th ionization energy of the cation (kJ mol\(^{-1}\)). Yellow triangles account for less than 10 coordination polyhedra; best fit equation for \(n \geq 10\) is given in text.

We also note a high correlation \((R^2 = 0.96)\) between the ratio \(\frac{R_o}{\langle R_{ij} \rangle_{\text{CN}}}\) (see equation 5) and Lewis acidity (Table 1)

\[
\frac{R_o}{\langle R_{ij} \rangle_{\text{CN}}} = 1 + 1.863 \ln S_a \quad \text{(eq.8)}
\]

for the 22 cations with \(n \geq 10\) coordination polyhedra for which bond-length data are available to calculate said ratio. This shows strong dependence of bond-valence parameter \(R_o\) on the Lewis acidity of the cation.

**Bond-length variation**

We generally observe much narrower bond-length ranges for nitrides than we do for oxides and oxysalts. This observation is likely due to a combination of the nascent sampling of the compositional space of inorganic nitrides and a focus by experimentalists on simple compositions and structures as a result of the significant challenges associated with synthesizing and growing these compounds. In fact, of the 18 transition metal configurations with bond-length range > 0.75 Å when bonded to \(\text{O}^{2-}\),\(^\text{50}\) only three configurations are observed in our dataset for nitrides: \(\text{\text{Mn}^{2+}}\) (\(n = 6\), with bond lengths 2.170 -2.417 Å; \(\text{\text{Cu}^{2+}}\) (\(n = 3\), with bond lengths 1.879-2.722 Å, and \(\text{\text{Nb}^{5+}}\) (\(n = 2\), with bond lengths 2.123 -2.129 Å; this compares to bond-length ranges of 0.837, 0.893 and 0.777 Å when bonded to \(\text{O}^{2-}\),\(^\text{50}\) respectively. Furthermore, the absence of any substantial bond-length variation in many ion configurations bonded to \(\text{N}^{3-}\) is a result of their observation in (relatively) highly-symmetrical structures with inherently little to no variation in a priori bond lengths; variation in a priori bond lengths was recently demonstrated to be the most common cause of bond-length variation in inorganic solids by Gagné & Hawthorne.\(^\text{50}\)

There are 66 cations overlapping this work and that of Gagné & Hawthorne for oxides\(^\text{50,61-64}\) from which we can directly compare mean bond-length and average observed coordination number. We find that cation-\(\text{N}^{3-}\) mean bond-lengths are on average 0.027 Å longer than their \(\text{O}^{2-}\) counterparts (0.034 Å when weighting these differences by the number of \(\text{N}^{3-}\) coordination polyhedra per cation) with mean bond-length differences varying between 0.318 Å

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shorter (Ag\(^+\)) and 0.196 Å longer (Hf\(^4+\)) when bonded to N\(^3-\). The average observed coordination number is 1.078 lower for cations bonded to N\(^3-\) vs O\(^2-\) (1.159, weighted).

Comparing the data on the basis of ion configurations (i.e., as a function of oxidation state and coordination number), the average increase in mean bond-length for N\(^3-\) coordination polyhedra is 0.118 Å (0.106 Å when weighting these differences by the number of N\(^3-\) coordination polyhedra per cation), over 112 overlapping ion configurations. In comparison, the ionic radii for \([\text{N}^3-]^{\text{10}}\) and \([\text{O}^2-]^{\text{10}}\) are 1.46 and 1.38 Å, respectively.\(^{60}\) Thus, our data show a slightly more pronounced increase in mean bond-lengths for N\(^3-\) vs O\(^2-\) than predicted via the addition of ionic radii, with the largest increase for \([\text{Hg}^2+]\) (0.339 Å) and largest decrease for \([\text{Ag}^+\) (-0.120 Å).

We do not observe structures with N-H...N complexes in our neutron diffraction dataset; only N-H...O (n = 25) and O-H...N (n = 4). For N-H bonds, the average length is 0.999 Å with a range of 0.915-1.025 Å; for N-H bonds, the average length is 2.269 Å, with a range of 2.034-2.610 Å.

**Anomalous bond-length distributions**

Bond lengths are expected to form positively-skewed Gaussian distributions as a result of the interplay between Coulomb attraction and Born repulsion for ion pairs (Fig. 3c gives such an example for \([\text{IC}^2+]\) bonded to N\(^3-\)). Gagné & Hawthorne state that deviations from such shape are the result of bond-topological, electronic and/or crystal-structure effects,\(^{59}\) which they go on to describe for all cations of the periodic table observed bonding to O\(^2-\) in inorganic structures.\(^{61-64}\) Notable examples of anomalous bond-length distributions include a tri-modal distribution for \([\text{P}^3+]\)-O\(^2-\) bonds,\(^{65}\) caused by varying bond-valence requirements as a function of the degree of polymerization of the \([\text{PO}_x]^{3-}\) oxyanion (i.e. bond-topological effects), a tri-modal distribution for \([\text{Mo}^{6+}\)O\(^2-)\) bonds,\(^{50}\) arising from a combination of pseudo Jahn-Teller and bond-topological effects, and anomalously long tails at longer bond lengths for penta-coordinated ion configurations of Cr\(^{2+}\), Co\(^{2+}\) and Cu\(^{2+}\), also caused by pseudo Jahn-Teller and bond-topological effects.\(^{50}\)

Fig. 3 shows bond-length distributions for the data of Table 2 (cations bonded solely to N\(^3-\)) for n > 100 bond lengths and a few more interesting configurations. Due to a general paucity of data, partly due to the difficulty of growing inorganic nitrides as single crystals, few ion configurations have sufficient data for a distinct shape to arise from their bond-length distribution.

**Table 2: Bond-length statistics for cations bonded to N\(^3-\)**

| Ion | Coordination number | Number of coordination polyhedra | Number of bonds | Mean bond-length (Å) | Standard deviation (Å) | Range (Å) | Maximum bond-length (Å) | Minimum bond-length (Å) |
|-----|---------------------|---------------------------------|----------------|----------------------|------------------------|-----------|------------------------|------------------------|
| H\(^+\) | 2          | 0 (29)                          | 0 (58)         | 1.947                | 0.025                  | 0.078     | 1.990                  | 1.912                  |
|       | 3          | 0 (1)                           | 0 (3)          |                      |                        |           |                        |                        |
| Li\(^+\) | 2         | 11                              | 22             | 2.121                | 0.029                  | 0.125     | 2.181                  | 2.056                  |
|       | 3         | 12                              | 36             |                      |                        |           |                        |                        |
|        | 4          | 43 (10)                         | 172 (40)       | 2.148                | 0.103                  | 0.690     | 2.613                  | 1.923                  |
|        | 5          | 2 (2)                           | 10 (10)        | 2.240                | 0.185                  | 0.681     | 2.722                  | 2.041                  |
|        | 6          | 3                               | 18             | 2.255                | 0.039                  | 0.094     | 2.302                  | 2.208                  |
| Be\(^{2+}\) | 3       | 1                              | 3              | 1.660                | 0.026                  | 0.059     | 1.683                  | 1.624                  |
|        | 4          | 1                               | 4              | 1.746                | 0.014                  | 0.038     | 1.770                  | 1.732                  |
| B\(^3+\) | 2         | 31                              | 62             | 1.337                | 0.017                  | 0.096     | 1.383                  | 1.287                  |
|       | 3         | 12 (3)                          | 36 (9)         | 1.473                | 0.029                  | 0.143     | 1.545                  | 1.402                  |
|        | 4          | 4 (1)                           | 16 (4)         | 1.557                | 0.019                  | 0.052     | 1.570                  | 1.518                  |
| C\(^4+\) | 2         | 33 (4)                          | 66 (8)         | 1.226                | 0.061                  | 0.188     | 1.325                  | 1.137                  |
|       | 3         | 103 (130)                       | 309 (390)      | 1.326                | 0.017                  | 0.119     | 1.395                  | 1.276                  |
| N\(^5+\) | 2         | 2                              | 4              | 1.194                | 0.000                  | 0.000     | 1.194                  | 1.194                  |
|       | 3         | 0 (4)                           | 0 (12)         |                      |                        |           |                        |                        |
| Na\(^+\) | 4        | 6 (5)                           | 24 (20)        | 2.417                | 0.052                  | 0.200     | 2.538                  | 2.338                  |
|       | 5        | 12 (7)                          | 60 (35)        | 2.594                | 0.196                  | 0.783     | 3.116                  | 2.333                  |
|       | 6        | 16 (26)                         | 96 (156)       | 2.562                | 0.113                  | 0.640     | 3.022                  | 2.382                  |
| Mg\(^2+\) | 4       | 4                               | 16             | 2.121                | 0.049                  | 0.162     | 2.198                  | 2.036                  |
|    | 6   | 0 (3) | 0 (18) | 1.898 | 0.043 | 0.144 | 1.984 | 1.840 |
|----|-----|-------|--------|-------|-------|-------|-------|-------|
| Al³⁺ | 4   | 9     | 36     | 2.044 | 0.006 | 0.015 | 2.052 | 2.037 |
| Si⁴⁺ | 4   | 46 (11) | 184 (44) | 1.738 | 0.039 | 0.288 | 1.941 | 1.653 |
| P⁵⁺ | 4   | 28 (52) | 112 (208) | 1.624 | 0.030 | 0.151 | 1.711 | 1.560 |
| S⁶⁺ | 2   | 9 (1) | 18 (2) | 1.552 | 0.020 | 0.069 | 1.596 | 1.527 |
| S⁰ | 4   | 0 (46) | 0 (184) | 2.044 | 0.006 | 0.015 | 2.052 | 2.037 |
| K⁺ | 4   | 1     | 4     | 2.044 | 0.006 | 0.015 | 2.052 | 2.037 |
| Ca²⁺ | 4   | 9     | 36     | 2.491 | 0.031 | 0.115 | 2.526 | 2.411 |
| V²⁺ | 6   | 1     | 6     | 2.224 | 0.000 | 0.000 | 2.224 | 2.224 |
| V³⁺ | 3   | 1     | 3     | 1.815 | 0.007 | 0.017 | 1.825 | 1.808 |
| Mn³⁺ | 3   | 1     | 3     | 1.760 | 0.025 | 0.155 | 1.823 | 1.794 |
| Mn⁵⁺ | 4   | 2     | 8     | 1.637 | 0.032 | 0.095 | 2.166 | 2.071 |
| Fe²⁺ | 3   | 1     | 4     | 1.899 | 0.026 | 0.080 | 1.941 | 1.861 |
| Fe³⁺ | 6   | 9 (2) | 54 (12) | 2.196 | 0.032 | 0.128 | 2.274 | 2.146 |
| Co⁺ | 2   | 1     | 2     | 1.749 | 0.000 | 0.000 | 1.749 | 1.749 |
| Co²⁺ | 4   | 5     | 16    | 1.963 | 0.011 | 0.035 | 1.983 | 1.948 |
| Co³⁺ | 6   | 36 (30) | 216 (180) | 1.963 | 0.013 | 0.115 | 2.007 | 1.892 |
| Element | Value | Charge | Charge | Atomic Weight | Oxidation State | Atomic Weight | Oxidation State |
|---------|-------|--------|--------|---------------|----------------|---------------|----------------|
| Ni^{2+} | 4     | 10     | 40     | 1.928         | 0.025          | 0.141         | 2.014          | 1.873          |
|         | 6     | 4 (5)  | 24 (30)| 2.127         | 0.026          | 0.085         | 2.164          | 2.079          |
| Cu^{+}  | 2     | 8      | 16     | 1.875         | 0.022          | 0.084         | 1.931          | 1.847          |
|         | 4     | 1      | 4      | 1.977         | 0.000          | 0.000         | 1.977          | 1.977          |
| Cu^{2+} | 4     | 1 (1)  | 4 (4)  | 1.941         | 0.012          | 0.032         | 1.953          | 1.921          |
|         | 5     | 0 (2)  | 0 (10)|               |                |               |                |                |
| Zn^{2+} | 2     | 3      | 6      | 1.860         | 0.013          | 0.032         | 1.874          | 1.842          |
|         | 4     | 23 (2)| 92 (8)| 1.984         | 0.038          | 0.180         | 2.086          | 1.906          |
|         | 6     | 1      | 6      | 2.136         | 0.000          | 0.000         | 2.136          | 2.136          |
| Ga^{3+} | 4     | 3      | 12     | 1.952         | 0.040          | 0.159         | 2.063          | 1.904          |
|         | 6     | 1      | 6      | 2.079         | 0.012          | 0.035         | 2.099          | 2.064          |
| Ge^{4+} | 4     | 0 (2)  | 0 (8)  |               |                |               |                |                |
| Se^{6+} | 4     | 0 (2)  | 0 (8)  |               |                |               |                |                |
| Rb^{+}  | 6     | 6      | 36     | 3.080         | 0.104          | 0.441         | 3.347          | 2.906          |
|         | 7     | 1 (1)  | 7 (7)  | 3.085         | 0.099          | 0.315         | 3.191          | 2.876          |
|         | 8     | 14 (3)| 112 (24)| 3.263       | 0.193          | 0.806         | 3.764          | 2.958          |
|         | 9     | 0 (1)  | 0 (9)  |               |                |               |                |                |
| Sr^{2+} | 4     | 9      | 36     | 2.641         | 0.030          | 0.137         | 2.682          | 2.545          |
|         | 5     | 6      | 30     | 2.691         | 0.122          | 0.460         | 2.940          | 2.480          |
|         | 6     | 9 (1)  | 54 (6)| 2.749         | 0.150          | 0.708         | 3.216          | 2.508          |
|         | 7     | 1 (1)  | 7 (7)  | 2.916         | 0.229          | 0.601         | 3.221          | 2.620          |
|         | 8     | 1 (1)  | 8 (8)  | 2.977         | 0.299          | 0.811         | 3.379          | 2.568          |
|         | 10    | 2      | 20     | 2.999         | 0.248          | 0.810         | 3.380          | 2.570          |
|         | 13    | 1      | 13     | 3.268         | 0.311          | 1.024         | 3.730          | 2.706          |
| Y^{3+}  | 6     | 5      | 30     | 2.394         | 0.050          | 0.174         | 2.478          | 2.304          |
| Nb^{5+} | 4     | 10     | 40     | 1.963         | 0.024          | 0.110         | 2.026          | 1.916          |
|         | 6     | 2      | 12     | 2.126         | 0.003          | 0.006         | 2.129          | 2.123          |
| Mo^{6+} | 4     | 11 (1)| 44 (4)| 1.864         | 0.031          | 0.149         | 1.951          | 1.802          |
|         | 5     | 0 (1)  | 0 (5)  |               |                |               |                |                |
| Ru^{3+} | 6     | 8      | 48     | 2.092         | 0.005          | 0.019         | 2.101          | 2.082          |
| Rh^{3+} | 6     | 3 (2)  | 18 (12)| 2.071         | 0.007          | 0.024         | 2.078          | 2.054          |
| Pd^{2+} | 4     | 5      | 20     | 2.044         | 0.015          | 0.060         | 2.079          | 2.019          |
| Ag^{+}  | 2     | 9 (2)  | 18 (4)| 2.125         | 0.026          | 0.108         | 2.192          | 2.084          |
|         | 3     | 2      | 6      | 2.266         | 0.099          | 0.295         | 2.445          | 2.150          |
|         | 4     | 2      | 8      | 2.277         | 0.024          | 0.085         | 2.316          | 2.231          |
|         | 5     | 0 (1)  | 0 (5)  |               |                |               |                |                |
|         | 6     | 0 (2)  | 0 (12)|               |                |               |                |                |
| Cd^{2+} | 6     | 4 (4)  | 24 (24)| 2.341         | 0.044          | 0.227         | 2.466          | 2.239          |
| Sn^{2+} | 3     | 1      | 3      | 2.143         | 0.019          | 0.042         | 2.170          | 2.128          |
| Sn^{4+} | 6     | 4      | 24     | 2.177         | 0.000          | 0.001         | 2.178          | 2.177          |
| Element | Charge | Valence | Ionization Energy | Radii | Scattering Power |
|---------|--------|---------|------------------|-------|------------------|
| Cs⁺     | 6      | 1       | 3.187            | 0.000 | 0.000            |
|         | 7      | 2       | 3.342            | 0.135 | 0.393            |
|         | 8      | 5 (1)   | 3.396            | 0.146 | 0.641            |
|         | 9      | 2 (1)   | 3.479            | 0.242 | 0.839            |
|         | 10     | 5       | 3.559            | 0.263 | 0.836            |
|         | 11     | 1       | 3.665            | 0.242 | 0.698            |
|         | 12     | 5 (1)   | 3.642            | 0.145 | 0.448            |
| Ba²⁺    | 4      | 1       | 2.738            | 0.065 | 0.155            |
|         | 5      | 6 (1)   | 2.868            | 0.088 | 0.388            |
|         | 6      | 13 (1)  | 2.896            | 0.156 | 0.768            |
|         | 7      | 16      | 2.960            | 0.177 | 0.771            |
|         | 8      | 7       | 3.059            | 0.234 | 0.846            |
|         | 9      | 0 (3)   | 0.000            | 0.000 | 0.000            |
|         | 10     | 0 (3)   | 0 (27)           |       |                 |
|         | 11     | 0 (1)   | 0 (11)           |       |                 |
|         | 14     | 1       | 3.293            | 0.226 | 0.665            |
| La³⁺    | 6      | 1 (1)   | 2.531            | 0.006 | 0.013            |
|         | 7      | 1 (1)   | 2.607            | 0.151 | 0.397            |
|         | 8      | 8 (3)   | 2.698            | 0.104 | 0.553            |
|         | 9      | 3 (3)   | 2.770            | 0.154 | 0.621            |
| Ce³⁺    | 8      | 3 (2)   | 2.646            | 0.120 | 0.486            |
|         | 9      | 2 (4)   | 2.740            | 0.192 | 0.713            |
| Ce⁴⁺    | 6      | 1       | 2.427            | 0.000 | 0.000            |
| Pr³⁺    | 7      | 1       | 2.572            | 0.081 | 0.236            |
|         | 8      | 0 (1)   | 0 (8)            |       |                 |
| Nd³⁺    | 6      | 2       | 2.497            | 0.062 | 0.164            |
|         | 8      | 1 (3)   | 2.589            | 0.005 | 0.010            |
|         | 9      | 0 (2)   | 0 (18)           |       |                 |
| Sm³⁺    | 7      | 1       | 2.477            | 0.046 | 0.162            |
|         | 8      | 0 (5)   | 0 (40)           |       |                 |
|         | 9      | 0 (1)   | 0 (9)            |       |                 |
| Eu²⁺    | 6      | 2       | 2.599            | 0.106 | 0.279            |
|         | 8      | 1       | 2.861            | 0.256 | 0.681            |
|         | 10     | 1       | 2.928            | 0.214 | 0.717            |
|         | 12     | 1       | 2.993            | 0.048 | 0.135            |
| Eu³⁺    | 6      | 1       | 2.463            | 0.002 | 0.003            |
|         | 8      | 0 (1)   | 0 (8)            |       |                 |
| Gd³⁺    | 9      | 0 (2)   | 0 (18)           |       |                 |
| Tb³⁺    | 8      | 0 (3)   | 0 (24)           |       |                 |
| Dy³⁺    | 8      | 0 (1)   | 0 (8)            |       |                 |
| Ho³⁺    | 6      | 1       | 2.417            | 0.104 | 0.274            |
|         | 8      | 0 (1)   | 0 (8)            |       |                 |
Inspection of these bond-length distributions and of their constituent anomalous bond lengths paints inorganic nitrides as chemically inconspicuous compared to oxides and oxysalts (however, we remind the reader that many nitride structures have been refined via powder XRD and are consequently not accounted for in this work). Only a few ion configurations are observed with irregularities. For the [2]C4+ configuration (Fig. 3c), we observe a tri-modal distribution of bond lengths with peaks at ~1.15, ~1.22 and ~1.31 Å. Converting these bond lengths into bond valences results in peaks at ~1.15, ~1.22 and ~1.31 Å. The bond valence sum ~1.22 Å arises from symmetrical bonds of N≡C≡N cyanamide units, such as in the structure of SrCN2 (75040) with a priori (observed) bond valences 2 × 2 v.u. (1.933 and 1.985) for C4+ (6 × 1/3 v.u. for Sr2+) calculated using the method of Gagné & Hawthorne72 (Table S2). The two other peaks of Fig. 3c are complementary, with bond-valence sum ≈ 4 v.u.; they result from N-C≡N cyanamide units, for example in AgN(CN)2, 843 with a priori (observed) bond valences 1.5 (1.524) and 2.5 (2.626) v.u. for C4+, and 2 × 0.5 (0.511) v.u. for Ag+. Thus, this result shows that bond valences are not perfectly distributed into a [3+1] v.u. arrangement in cyanamide units; a bond-valence of 3 v.u. would require a bond length of 1.115 Å.

Two other bond-length distributions are observed with slight irregularities; those of [4]P5+ and [6]W6+ (Fig. 3f and 3k, respectively). In both instances, the root cause for irregularity is bond-topological asymmetry. For these ion configurations, competition between the bond-valence constraints of the cation and its bonded anions requires uneven distribution of bond valences (thus bond lengths; eq. 1) in cation and/or anion coordination polyhedra. This mechanism of bond-length variation was described for [6]P5+ bonded to O2- by Gagné & Hawthorne62 and was later extended to transition metals and described under the umbrella of bond-topological effects.50 For example, [4]P5+ ideally forms 4 bonds that are 1.25 v.u. in strength; however, the ideal bond strengths for a bridging [2]N3- ion are 2 × 1.5 v.u. Thus, for polymerization into corner-sharing dimers, [4]P5+ adapts to the bond-valence requirement of [2]N3- and increase the strength of one bond to 1.5 v.u., weakening the three other bonds to 1.167 v.u. For a chain of corner-sharing tetrahedra, [6]W6+ adjusts to 2 × 1.5 and 2 × 1 v.u. — so and so forth for different combinations of degrees of polymerization, number of shared vertices, and varying coordination number of the bridging anion(s). These different combinations result in multiple maxima in the bond-length distribution of cations prone to bond-topological effects, and a complete description of the shape of their bond-length distributions is achieved via the calculation of a priori bond valences for their constituent crystal structures. In our dataset, [6]P5+ and [6]W6+ are observed to polymerize into oligomers, chains, rings, sheets, clusters and frameworks; we do not resolve the bond-valence requirements of each scenario here. Other subtle instances of multi-modality observed in Fig. 3 result from paucity of data.

In the next part of this work, we examine structural and electronic effects accounting for anomalous bond lengths in our dataset, and further discuss certain effects of technological importance observed or yet to be observed in inorganic nitrides. Thus, we shift our focus toward uncovering less traditional bonding properties of inorganic nitrides that offer promising opportunities in the exploration of their compositional space.
Figure 3: Bond-length distributions for selected ion configurations bonded to N\textsuperscript{3}: (a) \textsuperscript{[4]}Li\textsuperscript{+}, (b) \textsuperscript{[2]}C\textsuperscript{4+}, (c) \textsuperscript{[3]}C\textsuperscript{4+}, (d) \textsuperscript{[6]}Na\textsuperscript{+}, (e) \textsuperscript{[4]}Si\textsuperscript{4+}, (f) \textsuperscript{[4]}P\textsuperscript{5+}, (g) \textsuperscript{[6]}K\textsuperscript{+}, (h) \textsuperscript{[6]}Co\textsuperscript{3+}, (i) \textsuperscript{[6]}Rb\textsuperscript{+}, (j) \textsuperscript{[7]}Ba\textsuperscript{2+}, (k) \textsuperscript{[8]}W\textsuperscript{6+}.

Opportunities for exploratory synthesis
On the exploration of new compositional spaces

This past decade has seen a rapid increase in the development of high-throughput (HT) computational methods applied to materials discovery. These methods, usually rooted in Density Functional Theory (DFT) and/or Machine Learning (ML), allow screening of large compositional spaces in search of yet-to-be-observed compounds with desired functional properties. A growing number of HT studies include experimentally-validated predictions (see a list compiled by Jain et al. for DFT\textsuperscript{86}–\textsuperscript{92} partly owing to their suitability to synthesizability analysis\textsuperscript{3,21,93,94} — an emerging concept used to curb the difficulty of predicting the outcome of chemical reactions in the solid state.

Today, rapid increase in available computational power has by-and-large transformed the problem of \textit{in silico} exploration from one of computational feasibility to one of \textit{a priori} identifying compositional spaces of interest\textsuperscript{95,96} — a pursuit that has historically been realized via rules of crystal
chemistry\textsuperscript{97,98} and heuristic concepts. However, several issues cloud the exploration of new compositional spaces via DFT approaches, separate from the difficulties traditionally associated with the theory itself (e.g. strongly-correlated systems, substitutional disorder, ground state calculations that ignore a potentially non-negligible entropic contribution to structure stability,\textsuperscript{99} etc.). For example, while exploration of extensive compositional spaces is currently manageable for ternary phases (as most recently evidenced by the work of Sun et al.\textsuperscript{21}), quaternary-and-higher compositional spaces are exponentially-more computationally-expensive for they require their stability be evaluated against an exponentially-large number of stoichiometrically-feasible phases of lower order. Current approaches are further limited to a relatively small set of known elementary, binary, and ternary crystal structures which may not necessarily conform to the chemical compositions investigated. Nonetheless, these problems are largely temporal, and should progressively lessen with an ever-increasing supply of computational power and the incremental discovery of new crystal structures.

A more difficult (yet hardly discussed) problem is the fundamental inability of DFT to model energetically-degenerate and pseudo-degenerate electronic states, whereby vibronic coupling giving rise to Jahn-Teller (and pseudo Jahn-Teller) distortions do not conform to the Born-Oppenheimer and adiabatic approximations underpinning DFT.\textsuperscript{100,101} This is problematic with regard to the starting extent to which vibronic coupling occurs in inorganic solids, as recently shown by Gagné & Hawthorne via large-scale bond-length dispersion analysis for oxides and oxysalts;\textsuperscript{50} of 147 configurations of transition metal ions observed bonding to O\textsuperscript{2−}, 52 configurations were observed with anomalous bond-length distributions, 46 of which partially or entirely due to vibronic coupling. Complementing DFT calculations with other approaches could attenuate this problem; for example, prediction of non-centrosymmetric behavior is within the purview of machine learning, which has been used in combination with DFT calculations to insulate promising non-centrosymmetric compositions from large compositional spaces (e.g. Ruddlesden-Popper oxides\textsuperscript{102}). The practice of combining DFT and machine learning approaches was recently reviewed by Schleder et al.\textsuperscript{103}

Notwithstanding the above, HT computing should not be mistaken for a one-stop solution to the multi-faceted issue of exploratory synthesis.\textsuperscript{104} While HT methods play a critical role in fast-tracking materials discovery via the identification of "missing compounds" and the calculation of their properties,\textsuperscript{21,95} they are limited to rehashing data derived from known chemical spaces; navigating the totality of all existing chemical and structural spaces is categorically intractable for state-of-the-art HT methods.\textsuperscript{105} Thus, the discovery of new compositional spaces and of next-generation materials largely continues to lie in the ingenuity of the crystal and synthetic chemists. This assertion is particularly relevant to the exploration of inorganic nitrides, whose remarkable range of metastability suggests an exceptionally broad spectrum of observable compositions.\textsuperscript{93} Combined with the main takeaways of our bond-length dispersion analysis, this proposition leads us to affirm that the chemical potential of inorganic nitrides has barely been scratched, thus pressing the need for exploration outside known compositional spaces.

**New compositional spaces for the exploratory synthesis of nitrides**

In light of the recent extensive review of the crystal chemistry of oxides and oxysalts by Gagné & Hawthorne,\textsuperscript{50,61–64} we investigate our dataset of inorganic nitride structures for the occurrence of bond topological, electronic and/or crystal-structure effects, placing emphasis on the functional properties resulting from these effects. Compositional and structural divergences are expected between the compounds making up these two datasets. For example, lower cation coordination numbers are expected in inorganic nitrides due to the larger size of N\textsuperscript{3−} vs O\textsuperscript{2−} (as evidenced by our comparison of mean bond lengths between N\textsuperscript{3−} and O\textsuperscript{2−} structures, above). We further expect similar or lower oxidation states for cations in inorganic nitrides since O\textsuperscript{2−} is better at stabilizing high metal oxidation states as a result of its higher electronegativity (3.44 vs 3.04 for N).\textsuperscript{106} Furthermore, the reduced ionicity of the chemical bonds made by N\textsuperscript{3−} allows formation of exceptionally strong and localized bonds that can lock-in energetically unfavorable atomic arrangements;\textsuperscript{93} this is particularly relevant to electronegative p-block and d-block elements.

We further examine the chemical behavior of inorganic nitrides in coordination complexes; many molecular features of coordination complexes are preserved as they incorporate into crystal structures, and the carrying of their electronic properties is often more important than the steric constraints of space-group symmetry and long-range order.\textsuperscript{107} A chemically-intuitive treatment of chemical bonding thus follows from the common simplifying assumption of no translational symmetry,\textsuperscript{108,109} allowing the study of molecular fragments via Ligand Field theory. The slight loss in accuracy (effectively, losing information on “additional” bonding schemes that arise in extended solids as a result of electron delocalization) is greatly overcome by substantial gains in chemical intuition at a local scale, resulting in transferable insight useful to the exploration of new compositional spaces. As such, bonding knowledge derived in coordination chemistry poses as powerful inspiration to solid-state syntheses.\textsuperscript{110}

We organize our discussion into five phenomenological compositional spaces holding promise for the exploratory synthesis of functional inorganic nitrides. In contrast to HT methods, the intent of the following subsections is not to identify specific chemical compositions and/or crystal structures, but to unearth new and promising compositional spaces from an otherwise intractable combinatorial space of chemistries.

**Multiple-bond formation**

One of the primary causes of bond-length variation in inorganic solids is the formation of “multiple bonds” between ion pairs.\textsuperscript{50} Inorganic nitrides are exciting materials for in-depth study of this phenomenon and its ensuing properties, for they are a rare class of solid-state compounds where triple-bond formation (i.e. up to 3 v.u. in strength) is possible. In inorganic nitrides, multiple-bond formation is commonly observed for metal nitrido complexes, i.e. coordination...
complexes which contain one or more atoms of nitrogen bound only to transition metals. In these complexes, multiple-bond formation (commonly called "double" or "triple" bonds) occurs via mixing of anion p orbitals and unfilled metal d and/or for orbitals.111,112

Coordination compounds containing nitrido complexes are ubiquitous in chemical literature, largely driven by the desire to improve our understanding of the mechanism of nitrogen fixation (which is assumed to undergo nitrido-complex formation).113 Comprehensive reviews bring into light the remarkable chemical versatility of doubly- and triply-bonded N3.114–118 Despite this wealth of information, very few compounds containing double or triple M-N bonds have been synthesized and characterized in the solid state.

Of the 137 cation configurations we observe bonded solely to N3 (Table 2), only four configurations are observed with one or more structures containing a bond valence > 1.95 v.u.; three are non-metals, the other is [4]W6+ (including oxynitrides only adds one configuration to this tally: [3]Mo6+). In comparison, Gagné & Hawthorne report 15 of 461 cation configurations with bond valence > 1.95 v.u. (i.e. discrete terminal double bonds to O2−) in oxide and oxysalt structures.50 Although inorganic nitrides have the ability to make terminal bonds up to 3 v.u. in strength, we observe no such bonds in our dataset. The strongest metal bond observed is for [5]Mo6+ in oxynitride Na2Mo6+O4N139 (55113) with a Mo6+-N3 distance of 1.719 Å, representing a bond valence of 2.583 v.u.

Evidently, the potential for making strong terminal bonds to N3 is untapped; combined with the incredible variety of known nitrido complexes spanning most metals of the periodic table (including [1]112,129), doubly and triply-bonded inorganic nitrides are promising candidates for exploratory synthesis. Such compounds may not only be helpful in clarifying the mechanism of N2 reduction, but could possibly be used as heterogeneous catalysts in the development of a post-Haber-Bosch process proceeding at milder reaction conditions; the remarkable diversity of known nitrido-complex compounds shows considerable promise for fine tuning the kinetics of N2 and H2 activation. Metal-nitrido coordination complexes have also been reported as a key component to the catalytic oxidation of water,121 alkanes122,123, alkenes and alcohols,123 thus showing further promise for their use as solid-state catalysts.

There are 66 of 76 cations and 112 of 137 cation configurations overlapping this work and that of Gagné & Hawthorne for oxides and oxysalts,50,61–64 whereby non-overlapping configurations primarily result from the preference of inorganic nitrides for lower cation oxidation states and/or coordination numbers. Based on the similar crystal-chemical behavior of these classes of compounds, their significant overlap in cation configurations, and the isoelectronic nature of N3 and O2, we assume that cation configurations yet-to-be-observed in inorganic nitrides with equal or lower oxidation states and/or coordination numbers than their oxide and oxysalt counterparts either result from challenging synthesis or lack of synthetic attempts. Comparing the dataset of Gagné & Hawthorne against the present work for cation configurations with bonds > 1 v.u., we conclude that promising opportunities for multiple bond-formation (1-3 v.u.) in inorganic nitrides include cations such as Ti4+, V4+, As5+, Se1.6+, Br5+, Tc7+, Te6+, I7+, W5+, Re7+, Os6+, Bi6+; U6+ and Np6+; further work is also warranted for V4+, Cr1.6+, Nb5+, Mo6+, Ta5+ and W6+.

Coupled electronic-vibrational degeneracy: the Jahn-Teller effect

The Jahn-Teller effect (JTE) is a mechanism of symmetry-breaking that results from strong electron-vibrational (vibronic) and electron–phonon interactions in molecules and crystals, respectively,124 and is characterized by energetically-favorable occupancy of electronic states ensuing degeneracy-breaking polyhedral distortion. Although the JTE is commonly observed in coordination complexes of N3 (including nitrido complexes,125 with applications counting single-molecule magnets126), research into the material properties resulting from the JTE has historically focused on oxide and oxysalt compounds, including colossal magnetoresistance,127 superconductivity,128 improved electrochemical performance of cathode materials via the "opening" of diffusion channels,129,130 and magnetic-dielectric bistability.101

Gagné & Hawthorne’s recent bond-length dispersion analysis for transition metals bonded to O2 identifies 4 out of 52 typically highly-distorted ion configurations where coupled electronic-vibrational degeneracy is the principal underlying cause of bond-length variation, [6]Cr2+, [6]Mn4+, [6]Cu2+ and [6]Os7+, and an additional three configurations where it is a minor contributing factor: [6]Co2+, [6]V4+ and [6]Mo6+. Considering the lower electronegativity of N vs O (which entails more covalent bonds to transition metals) and the isoelectronic nature of these ligands, there is reason to believe that the above ion configurations (and possibly others) may experience the JTE with larger distortion magnitude when bonded to N3.

In the present dataset, we observe three cation configurations (bonded solely to N3) for which anomalous bond lengths can be attributed to the JTE: [3]Cr3+, [6]Co3+ (weak) and [6]Cu2+ (strong). Ion configurations [6]Mn4+, [6]Os7+ and [6]Mo6+ have yet to be observed, while [6]Cr2+ and [6]V4+ are each observed in one structure, refined as regular octahedra, and [6]Co2+ observed in two structures, also refined as regular octahedra. [3]Cr3+ is observed in Ca3Cr2+3N3 (40205) with bond lengths 2 × 1.766 and 1.863 Å.121 [6]Co3+ ([Ar]3d6) is observed in (NH3)12Co3+3NSi3+5(CN)3H2O (4094), with two anomalously short bond lengths of 1.907 and 1.932 Å. The Jahn-Teller (JT) effect identifies four structures containing an N3− ligand, where it is a minor contributing factor: [6]Co3+ (weak), [6]V4+ and [6]Mo6+. Considering the lower electronegativity of N vs O (which entails more covalent bonds to transition metals) and the isoelectronic nature of these ligands, there is reason to believe that the above ion configurations (and possibly others) may experience the JTE with larger distortion magnitude when bonded to N3.
The surprisingly large range of bond-length observed for the latter structure, 0.843 Å, appears to support the case for higher distortion magnitude in inorganic nitrides; of 365 polyhedra observed bonding to O\textsuperscript{2−} by Gagné & Hawthorne,\textsuperscript{9,90} only one is observed with a larger range of bond lengths, 0.870 Å, for mrázekite Bi\textsubscript{12}Cu\textsubscript{2}S\textsubscript{3}(OH)\textsubscript{4}O\textsubscript{2}(PO\textsubscript{4})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{6} (71934).\textsuperscript{137}

To verify that the large variation of bond lengths is not due (or partly due) to bond-topological asymmetry in K\textsubscript{3}CuFe(CN)\textsubscript{6} we calculate values of \(\Delta_{\text{topol}}\) and \(\Delta_{\text{cryst}}\) for the Cu\textsuperscript{2+}-N\textsubscript{6} octahedron using the method of Gagné & Hawthorne (2019); \(\Delta_{\text{topol}}\) is calculated as the mean (absolute) weighted deviation between the bond valences of a given polyhedron and that of its regular variety with equidistant bond lengths, i.e. its Pauling bond strength, and \(\Delta_{\text{cryst}}\) is calculated as the mean (absolute) weighted deviation between the \textit{a priori} and observed bond valences — thus encompassing all effects not arising from bond-topological arguments. We calculate \(\Delta_{\text{topol}} = 0.008\) and \(\Delta_{\text{cryst}} = 0.199\) v.u. for the Cu\textsuperscript{2+}-N\textsubscript{6} octahedron; these values clearly indicate that bond-length variation is overwhelmingly due to the JTE, supporting the suggestion of larger distortion magnitude for cations bonded to N\textsuperscript{3−} (\textit{a priori} bond valences are given in Table S2). The untapped potential for highly-distorted Cu\textsuperscript{2+} polyhedra (and other JT-active cations) may have important implications in the design of oxynitride and/or nitride counterparts to cuprate superconductors, with a handful of layered oxynitride\textsuperscript{138} and nitride superconductors already known for d\textsuperscript{0} transition metals.\textsuperscript{139,140}

Our dataset contains two cations that seem to be JT-active in octahedral coordination to N\textsuperscript{3−} with d\textsuperscript{0} and d\textsuperscript{1} electronic configurations: \textsuperscript{6}Co\textsuperscript{3+} and \textsuperscript{10}Co\textsuperscript{3+}. \textsuperscript{6}Co\textsuperscript{3+} ([Ar]d\textsuperscript{4}, n = 1) is observed in [Co\textsuperscript{2+}(NH\textsubscript{3})\textsubscript{6}]\textsubscript{2+} (78860)\textsuperscript{141} with reported high spin configuration, refined as a regular octahedron. \textsuperscript{10}Co\textsuperscript{3+} ([Ar]d\textsuperscript{7}, n = 2) is observed in [Co\textsuperscript{2+}(NH\textsubscript{3})\textsubscript{6}][PF\textsubscript{6}]\textsubscript{2−} (30704; spin unknown)\textsuperscript{142} with bond lengths 6 × 2.186 Å, nearly identical to those of [Co\textsuperscript{2+}(NH\textsubscript{3})\textsubscript{6}]Br\textsubscript{2} (78864)\textsuperscript{141} (6 × 2.176 Å) with Co\textsuperscript{2+} in high spin configuration. In comparison, both \textsuperscript{6}Co\textsuperscript{3+} and \textsuperscript{10}Co\textsuperscript{3+} are dominantly high spin in oxides,\textsuperscript{39} making \textsuperscript{10}Co\textsuperscript{3+} strongly JT-active (with clear-cut bimodal bond-length distribution) and \textsuperscript{6}Co\textsuperscript{3+} weakly JT-active (unimodal bond-length distribution). It is possible that the observation of regular Co\textsuperscript{2+}/Co\textsuperscript{2+}-N\textsubscript{6} octahedra is due to the dynamic JTE, which was shown to be present in Co\textsuperscript{2+}N\textsubscript{6} terpyridine complexes by Kremer et al.\textsuperscript{143} In oxynitride Co\textsuperscript{2+}(H\textsubscript{2}O)\textsubscript{2}Ni\textsuperscript{2+}(CN)\textsubscript{4}·4H\textsubscript{2}O (59366; spin unknown)\textsuperscript{144} bond distances are 2 × 2.095 and 2 × 2.101 Å to N\textsubscript{3−}, and 2 × 2.128 Å to O\textsuperscript{2−} (0.380, 0.376 and 0.319 v.u. respectively); in Cs\textsubscript{3}Co\textsuperscript{2+}(Sr(Re\textsuperscript{3+}(CN))\textsubscript{6})(H\textsubscript{2}O)\textsubscript{2} (89491)\textsuperscript{145} bond distances are 2.052 (0.390) and 2.092 (0.351) to O\textsuperscript{2−}, and 4 × 2.161 Å (0.332 v.u.) to N\textsubscript{3−}, indicating that \textsuperscript{6}Co\textsuperscript{3+} may be JT-active when bonded to a mixture of O\textsuperscript{2−} and N\textsubscript{3−}.

Other cations prone to the JTE and warranting further investigation include Fe\textsuperscript{3+}, Co\textsuperscript{3+}, V\textsuperscript{3+} and Mo\textsuperscript{3+} in octahedral coordination (weak); the observation of \textsuperscript{10}Mn\textsuperscript{3+} (strong) seems less likely as Mn\textsuperscript{3+} appears to prefer lower coordination numbers when bonded to N\textsubscript{3−}. Cations with lower coordination numbers (e.g. \textsuperscript{3}Fe\textsuperscript{3+} \textsuperscript{146}) do present further opportunity to study the JTE in inorganic nitrides, although bond-length variations associated with lower coordination numbers are usually modest.

### Coupled electronic-vibrational near-degeneracy: the pseudo Jahn-Teller effect

The pseudo Jahn-Teller effect (PJTE) is a mechanism of symmetry-breaking that results from the vibronic mixing of (two or more) electronic states sufficiently close in energy to interact under nuclear displacement.\textsuperscript{124,147} Vibronic mixing usually (but not necessarily) occurs between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), with a distortion mode having the same symmetry as the HOMO to LUMO transition.\textsuperscript{147} Although occurrence of the PJTE is not encumbered by \textit{a priori} limitations such as electronic configuration, the PJTE is primarily observed for d\textsuperscript{0} transition metals, with resulting non-centrosymmetric behavior responsible for a host of technologically-relevant properties including ferroelectricity,\textsuperscript{51,148} ferromagnetism,\textsuperscript{149} multiferroicity,\textsuperscript{150} piezoelectricity,\textsuperscript{51} photocatalysis,\textsuperscript{151} nonlinear optics,\textsuperscript{51,155} magnetic-dielectric bistability,\textsuperscript{103} etc. The PJTE is of particular interest to materials design, for the structural instability resulting from this effect can be controlled by means of electronic rearrangements induced by redox processes, electromagnetic fields, external pressure and more,\textsuperscript{147} with potential applications spanning bistable atomic switches,\textsuperscript{152-154} and control over sorption characteristics of catalysts to move beyond the Sabatier principle.

Because vibronic phenomena do not conform to the Born-Oppenheimer and adiabatic approximations, neither the JTE or PJTE are suited to DFT treatment.\textsuperscript{191} For this reason, the derivation of empirical trends and use of heuristic concepts is particularly important to the exploration of this phenomenon. Gagné & Hawthorne recently showed that the PJTE is the 2\textsuperscript{nd} most frequently encountered cause of bond-length variation in transition metals when bonded to O\textsuperscript{2−} (after bond-topological effects).\textsuperscript{39} In their work, the PJTE is observed as the main reason underlying anomalous bond-length distributions (in terms of shape and/or range) for 29 of 52 transition metal configurations, in addition to 11 ion configurations for which it is present in minor yet significant ways, covering electronic configurations d\textsuperscript{0}, d\textsuperscript{1}, d\textsuperscript{2}, d\textsuperscript{4} and d\textsuperscript{10}, and coordination numbers [4]-[10]. Because studies covering PJTE-active cations have almost exclusively focused on oxides and oxysalts, our understanding of this phenomenon is particularly lagging in inorganic nitrides, where few syntheses incorporating d\textsuperscript{0} transition metals have been attempted (with the exception of the group of Kazuhiko Maeda who studied a handful of oxynitrides with d\textsuperscript{0} transition metals as photocatalytic materials\textsuperscript{155}).

Because PJTE instabilities can be of any symmetry within the group representation, i.e., indiscriminate of coordination number, occurrence of the PJTE can be reduced to a problem of energy gap between interacting electronic states. In their study of octahedrally-coordinated d\textsuperscript{0} transition metals, Kunz & Brown\textsuperscript{156} observed an increasing degree of distortion with decreasing HOMO-LUMO gap, which in turn correlates to the size and charge of the d\textsuperscript{0} cation (this trend was later described in terms of electronegativity,\textsuperscript{157} whereby more electronegative cations lead to larger distortions when bonded to O\textsuperscript{2−}). While similar behavior is
expected for nitrides, the lower electronegativity of N (3.04) compared to O (3.44) entails a shift of the electronic states of N\(^{3+}\) to higher energies, thus affecting the HOMO-LUMO gap (and distortion magnitude) compared to O\(^{2-}\). As a result, the occurrence of PJT-driven distortion for bonds made to N\(^{3+}\) may be shifted to cations of lower electronegativity in relation to O\(^{2-}\) for a better match of orbital energies. In addition, the lower electronegativity of N (closer to that of transition metals) entails potential for larger distortion magnitude (measured as \(\Delta_{\text{cryst}}\)) owing to increased covalency of the M-N bond. However, others factors (e.g., nearest-neighbor identity\(^{147,157}\)) may have an overwhelming effect on the energy gap of the interacting states. While rationalizing the occurrence of the PJTE via quantum mechanical arguments is now commonplace, predicting the occurrence of a PJT distortion from simple crystal-chemical principles remains an open problem.

Table 3 summarizes bond-length information for ion configurations prone to the PJTE overlapping the present dataset and that of Gagné & Hawthorne for oxides and oxysalts.\(^{10}\) Italicised entries are for ion configurations where the PJTE is a minor contributor to bond-length variation in oxides and oxysalts, and are only shown for informational purposes (e.g., the effect of polymerization on bond length variation is much larger than that of the PJTE for \(\text{V}^{5+}\) when bonded to O\(^{2-}\)). To evaluate the relative distortion magnitude for cations bonded to N\(^{3+}\) vs O\(^{2-}\), one would ideally quantify the proportion of bond-length variation due to the PJTE via the method of Gagné & Hawthorne,\(^{50}\) i.e., by removing the bond-topological contribution to polyhedral distortion (example given in section above). Unfortunately, too few crystal structures are available to comprehensively calculate \(\Delta_{\text{topol}}\) and \(\Delta_{\text{cryst}}\) indices in inorganic nitrides. However, the few crystal structures suited to the calculation of these indices are in support of a shift of the occurrence of the PJTE to cations of lower electronegativity, and hint at larger distortion magnitude for the same ion configurations (data compared to Table S2 of Gagné & Hawthorne\(^{50}\)). For example, \(\Delta_{\text{topol}} = 0\) and \(\Delta_{\text{cryst}} = 0.177\) v.u. for \(\text{Hf}^{4+}\) in \(\text{Hf}^{5+}\text{N}_4\) (97997),\(^{158}\) with bond-length range 0.295 Å; in \(\text{Li}_2(\text{Ta}^{5+}\text{N}_3)\) (412585),\(^{159}\) \(\Delta_{\text{topol}} = 0.083\) and \(\Delta_{\text{cryst}} = 0.084\) v.u. for \(\text{Ta}^{5+}\), with bond-length range 0.106 Å. Distortion magnitudes attributable to the PJTE are still large for higher-electronegativity transition metals: in \(\text{LiBa}_2(\text{Mo}^{6+}\text{N})_3\) (74822),\(^{160}\) \(\Delta_{\text{topol}} = 0.079\) and 0.095 and \(\Delta_{\text{cryst}} = 0.230\) and 0.123 v.u. for two crystallographically-distinct \(\text{Mo}^{6+}\) sites, with bond-length ranges 0.149 and 0.111 Å, respectively; in \(\text{LiBa}_2(\text{W}^{6+}\text{N})_3\) (74823),\(^{160}\) \(\Delta_{\text{topol}} = 0.081\) and 0.091 and \(\Delta_{\text{cryst}} = 0.101\) and 0.064 v.u. for two crystallographically-distinct \(\text{W}^{6+}\) sites, with bond-length ranges 0.138 and 0.110 Å, respectively (all \(a\ priori\) bond valences in Table S2 herein).

Based on these observations, exploratory synthesis of PJTE-active inorganic nitrides appears promising for the subsequent exploitation of their functional properties. Common \(d^0\) transition metals warranting investigation and missing from our dataset include Sc\(^{3+}\), Ti\(^{4+}\), and Zr\(^{4+}\); these elements are particularly promising candidates for PJT-induced distortion in inorganic nitrides owing to their low electronegativity.

### Table 3: Comparison of mean bond-length ranges for PJTE-active cations bonded to N\(^{3+}\) vs O\(^{2-}\)

| Ion configuration | Electronic configuration | Sample size bonded to N\(^{3+}/O^{2-}\)† | Mean bond-length range bonded to N\(^{3+}/O^{2-}\) (Å) |
|-------------------|--------------------------|------------------------------------------|-----------------------------------------------|
| \([4]\text{V}^{5+}\)| \(d^0\)                   | 1/345                                     | 0.038/0.118                                    |
| \([4]\text{Cr}^{6+}\)| \(d^0\)                   | 2/169                                     | 0.024/0.120                                    |
| \([6]\text{Zn}^{2+}\)| \(d^{10}\)                  | 1/193                                     | 0/0.169                                        |
| \([6]\text{Y}^{3+}\)| \(d^0\)                   | 5/25                                      | 0.096/0.081                                    |
| \([4]\text{Nb}^{5+}\)| \(d^0\)                   | 10/2                                      | 0.049/0.117                                    |
| \([6]\text{Zn}^{2+}\)| \(d^{10}\)                  | 2/240                                     | 0/0.290                                        |
| \([4]\text{Mo}^{6+}\)| \(d^0\)                   | 11/434                                    | 0.068/0.069                                    |
| \([6]\text{Cd}^{2+}\)| \(d^{10}\)                  | 4/135                                     | 0.067/0.140                                    |
| \([8]\text{Hf}^{4+}\)| \(d^0\)                   | 1/7                                       | 0.295/0.163                                    |
| \([4]\text{Ta}^{5+}\)| \(d^0\)                   | 1/0*†                                     | 0.106/-                                       |
| \([4]\text{W}^{6+}\)| \(d^0\)                   | 26/35                                     | 0.124/0.053                                    |

*Oxide data taken from Gagné & Hawthorne (2019)

†Not observed bonded to O\(^{2-}\)

### Lone-pair stereoactivity

Lone-pair stereoactivity is an electronic phenomenon associated with the observation of highly anisotropic coordination polyhedra for p-block cations with \(ns^2np^6\) electron configuration. Lone-pair stereoactivity has been described as the causal mechanism for a multitude of material properties not limited to ultra-low thermal conductivity (a property most relevant to the development of next-generation thermoelectrics\(^{161,162}\), second-harmonic generation response,\(^{163–165}\) piezoelectricity,\(^{53,166}\) pyroelectricity,\(^{166,167}\) ferroelectricity,\(^{168,169}\) ferromagnetism,\(^{170}\) multiferricility,\(^{171}\) dielectric behavior,\(^{172}\) photocatalysis,\(^{151,173}\) and the photovoltaic effect.\(^{174}\)

Lone-pair (LP) stereoactivity originates from strong interaction between the cation and anion pairs leading to a high energy antibonding state which, via distortion of the structure, may interact with empty cation pairs to form a localized electronic state where the lone pair resides.\(^{175}\) As such, LP stereoactivity essentially amounts to a special case of the PJTE (see above), where crucial variables include a (vibronic) distortion mode with net positive overlap between the cation p and mixed cation s and anion p states, and favorable interaction between cation s and p states for the formation of the interacting antibonding states (the energy of which being strongly dependent on that of the anion p states). Thus, LP stereoactivity (vs inertness) is strongly a function of ligand identity; for example, the increasing energy of p states with increasing period has been demonstrated to reduce mixing with cation s states to the point of quenching the effect.\(^{176,177}\) Other factors influencing the occurrence and magnitude of lone-pair stereoactivity include the s character of the antibonding orbital (the higher the s character of the antibonding state, the better it is stabilized via mixing with the cation p state) and relativistic effects for period 6 cations, whereby relativistic
contraction of the 6s orbital reduces mixing with anion p states, leading to more diffuse lone pairs and less distorted structures.\textsuperscript{178}

Much like the PJTE, predicting the occurrence of LP stereoeactivity for a given composition/structure requires quantum mechanical analysis and eludes simple crystal-chemical principles; however, trends may be derived to maximize the probability of observing this phenomenon in new syntheses where composition and/or structure is not known \textit{a priori}. Trends in atomic orbital energy are most relevant in this regard. DFT calculations for a series of oxides have shown that the energy of O 2p state cuts in-between that of the s states of group 13 metals for periods 5 and 6 in way that leaves mixing with In\textsuperscript{3+} (group 14) unfavorable and Tl\textsuperscript{4+} (group 15) marginally favorable.\textsuperscript{175,179} Mixing becomes more favorable with increasing group number along these periods (i.e. with decreasing energy of the metal s state), making group 14 and 15 cations (Sn\textsuperscript{2+}/Sb\textsuperscript{3+} and Pb\textsuperscript{2+}/Bi\textsuperscript{3+}) most susceptible to stereoreactive lone-pair formation when bonded to O\textsuperscript{2-}. By this principle, the relatively higher-energy s state of period 4 p-block elements may be inferred to require further decrease in energy to best mix with the O 2p orbitals, thus making group 15 and 16 most prone to LP stereoeactivity (particularly As\textsuperscript{3+}) for this period. Such propositions are in-line with the results of the bond-length dispersion analysis of Gagné & Hawthorne for non-metals\textsuperscript{42} and metalloids/post-transition metals.\textsuperscript{43} With the 2p states of N being slightly more energetic than those of O (due to its lower electronegativity), we presume that LP stereoeactivity may be possible for cations with higher-energy states such as In\textsuperscript{3+}/Ge\textsuperscript{2+}, is most likely for elements Sn\textsuperscript{2+}, Pb\textsuperscript{2+}, As\textsuperscript{3+}, Sb\textsuperscript{3+} and Se\textsuperscript{4+}, and is least favorable for late-period, higher group elements.

There are unfortunately too few data available to resolve this issue; while literature abounds with well-characterized structures containing one or more stereoeactive lone pairs for oxides and oxysalts, and to a lesser extent chalcogenides and halides, surprisingly few structures have been reported with a stereoeactive lone pair when bonded to N\textsuperscript{3+}. Presumably, this paucity of data is due to the relatively nascent exploration of (functional) inorganic nitrates. Our dataset contains no data for As\textsuperscript{3+}, Se\textsuperscript{4+}, Sb\textsuperscript{3+}, Te\textsuperscript{4+} and Bi\textsuperscript{3+}. Only one coordination polyhedron was recorded for Sn\textsuperscript{2+}, in Li\textsubscript{2}(Sn(NH\textsubscript{3})\textsubscript{3}) (50467),\textsuperscript{180} with three short bonds 2.128, 2.132 and 2.170 Å in length and a stereoeactive lone pair occupying the 4\textsuperscript{th} apex of a tetrahedron. For period 6 ions, eight coordination polyhedra were recorded for Tl\textsuperscript{3+} and two for Pb\textsuperscript{2+}; in all cases, short bonds are concentrated in one hemisphere, away from the lone pair, while long bonds (if any) are present in the other. Thus, all p-block cations with ns\textsuperscript{2}np\textsuperscript{6} electron configuration are observed with a stereoeactive lone-pair in the present dataset, in sharp contrast to oxides and oxysalts; this result is promising for the exploitation of the functional properties resulting from lone-pair stereoeactivity in inorganic nitrates. Lone-pair stereoeactivity is further observed in coordination complexes for Ge\textsuperscript{2+},\textsuperscript{181} and in mixed coordination with Cl\textsuperscript{−} for Se\textsuperscript{4+}\textsuperscript{182} and Te\textsuperscript{4+},\textsuperscript{183,184} showcasing additional opportunity for the solid state.

### The (46)M\textsuperscript{6+} Configuration

Earth’s remarkable mineral diversity has been attributed to a number of factors spanning geochemical, crystal-chemical and thermodynamic considerations including efficient elemental concentration mechanisms, peculiar electronic behavior of certain elements, mineral stability ranges, etc.\textsuperscript{180,185,186} A less-discussed factor enabling mineral diversity is the ability of a (strongly-bonded) structural unit to polymerize into a variety of motifs (e.g. as oligomers, chains, rings, clusters, sheets, frameworks) inter-linked via weakly-bonded constituents. This concept is best illustrated for silicate minerals; there are currently 5510+ minerals approved by the International Mineralogical Association, 1540+ of which contain Si and O as essential elements (http://rruff.info/ima/). What are the salient characteristics of the SiO\textsubscript{4} unit that lead to such remarkable diversity? From the valence-sum rule (equation 2), we can deduce that the two bonds made by a bridging [2\textsuperscript{2}O\textsuperscript{2-} ion are ideally 1 v.u. in strength. Similarly, [4]Si\textsuperscript{4+} ideally makes four bonds 1 v.u. in strength. With the bond-valence requirements of [8]Si\textsuperscript{4+} perfectly matching those of [10]O\textsuperscript{2-} (see the valence-matching principle above), the SiO\textsubscript{4} unit freely polymerizes via one, two, three or four corners in a theoretically infinite number of motifs, leading to a remarkably stable and diverse class of minerals that accounts for ~90% of Earth’s crustal composition by volume.\textsuperscript{187} In inorganic nitrates, the analogous bond-valence requirements for a bridging [2\textsuperscript{2}N\textsuperscript{3-} anion are 2 × 1.5 v.u.; thus, hexavalent cations are required for polymerization of corner-sharing tetrahedra to result in proliferation of structural motifs (i.e. 4 × 1.5. v.u. = 6 v.u.), hence the significance of the (46)M\textsuperscript{6+} configuration in inorganic nitrates.

Porous materials (e.g. zeolites) are an important class of functional materials for which corner-sharing polymerization of the M\textsuperscript{6+}N\textsubscript{4} unit shows promise for exploratory synthesis. Zeolites are known for their remarkable catalytic and sorption characteristics,\textsuperscript{188,189} offering the ability to carry and optimize specific reactions via partial substitution of the cations making up the structural unit according to their Lewis acidity (Table 1).\textsuperscript{190} Although framework structures based on the M\textsuperscript{6+}N\textsubscript{4} unit have been synthesized,\textsuperscript{191} successful incorporation of N\textsuperscript{3-} as the major anion in a zeolite structure has so far only been achieved in the presence of stoichiometric oxygen for oxynitridophosphates (in NPO\textsuperscript{192} and NPT\textsuperscript{193}), and otherwise for zeolite-like (pore-less) nitridophosphates\textsuperscript{194} and nitridosilicates.\textsuperscript{195} Interestingly, framework structures based on the M\textsuperscript{6+}N\textsubscript{4} units may exhibit further interesting properties as a result of the pseudo Jahn-Teller effect for d\textsuperscript{0} transition metals such as Mo\textsuperscript{6+} and W\textsuperscript{6+} (e.g. ferroelectricity, ferromagnetism, piezoelectricity, magnetic-dielectric bistability; see above), thus possibly providing external control on molecular selectivity for catalytic reactions and adsorption/desorption processes.

Polymerization of the M\textsuperscript{6+}N\textsubscript{4} unit also shows promise for the synthesis of ultra-hard materials. The hardness of inorganic nitrides is known to be intimately linked to their bond strength;\textsuperscript{196,197} for example, the hardness of cubic BN (boron nitride), where all bonds are 0.75 v.u. in strength, is only slightly less than that of diamond (with bulk modulus 400 vs 440 GPA, respectively).\textsuperscript{198,199} Notwithstanding synthetic feats, the synthesis of M\textsuperscript{6+}N\textsubscript{2} nitrides with bonds 1.5 v.u. in
strength (e.g. Mo\textsuperscript{6+}N\textsubscript{2} and W\textsuperscript{6+}N\textsubscript{2}, analogous to SiO\textsubscript{2}) could lead to new ultrahard materials. In addition to their refractory nature, the characteristically high hardness of inorganic nitrides has already been applied to the development of reinforced cements and concretes for different forms of BN\textsuperscript{200,201}

We observe five ions with [4][M\textsuperscript{6+}] configuration in our dataset: S\textsuperscript{6+}, Cr\textsuperscript{6+}, Se\textsuperscript{6+}, Mo\textsuperscript{6+} and W\textsuperscript{6+}. Both the [4][S\textsuperscript{6+}] and [4][Se\textsuperscript{6+}] configurations are only observed in oxynitrizes thus far, either as [M\textsuperscript{6+}O\textsubscript{4}N\textsubscript{2}]\textsuperscript{6+} or [M\textsuperscript{6+}O\textsubscript{3}N\textsubscript{3}]\textsuperscript{6+}, while the [Cr\textsuperscript{6+}N\textsubscript{2}]\textsuperscript{6+} unit has yet to be observed as a product of polymerization. More interesting is the [WN\textsubscript{4}]\textsuperscript{6+} unit, which is observed to polymerize into dimers in Li\textsubscript{2}Ba\textsubscript{2}[W\textsubscript{6}N\textsubscript{4}]\textsubscript{2} (74823).\textsuperscript{160} 6-membered rings in K\textsubscript{2}W\textsubscript{6}N\textsubscript{4} (75033)\textsuperscript{202} chains in Na\textsubscript{2}Na\textsubscript{2}[W\textsubscript{6}N\textsubscript{4}]\textsubscript{2} (55534)\textsuperscript{203} sheets in Na\textsubscript{2}K\textsubscript{2}[W\textsubscript{6}N\textsubscript{4}] (81764)\textsuperscript{204} and into a framework structure in Cu\textsubscript{2}Na\textsubscript{2}[W\textsubscript{6}N\textsubscript{4}]\textsubscript{2} (50002)\textsuperscript{205} Fewer works have studied the polymerization of the [MoN\textsubscript{4}]\textsuperscript{6+} unit; dimers have been described in Li\textsubscript{2}Ba\textsubscript{2}[Mo\textsubscript{6}N\textsubscript{4}]\textsubscript{2}BaCl\textsubscript{2} (72400)\textsuperscript{206} and in Li\textsubscript{2}Ba\textsubscript{2}[Mo\textsubscript{6}N\textsubscript{4}]\textsubscript{2} (74822).\textsuperscript{160} Evidently, much of the potential of the [4][M\textsuperscript{6+}] configuration in inorganic nitrides lies ahead.

Conclusion

Following several decades of progressive syntheses primarily driven by new and improved methods of preparation, inorganic nitrides recently matured into a thriving class of inorganic solids with a promising set of functional properties akin to oxide and oxysalt compounds. This work utilizes known structure-property relationships to identify some of the most promising uncharted compositional spaces for these compounds which bear material properties, and provides basic parameters helpful to the design and characterization of these materials and to the verification of high-throughput computational results. Further developments for this class of materials will surely follow from strong symbiosis between theoretical, synthetic and computational chemists by way of identifying and understanding the structural underpinnings of their functional properties and energetics.

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ASSOCIATED CONTENT
Supporting information

Two tables cited in text (Table S1 and Table S2) listing structures used in anion bond-valence sum verification and a priori bond valences of selected crystal structures

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Notes
Relevant ICSD codes included in parentheses in text
ANOMALOUS BONDING BEHAVIOR OF N$^3$ → NEW CHEMICAL SPACES WITH PROMISING FUNCTIONAL PROPERTIES
## SUPPORTING INFORMATION

Table S1: ICSD code for the structures used in the anion bond-valence sum verification

| Cation | ICSD code |
|--------|-----------|
| H⁺     | 63027     |
| Li⁺    | 67560     |
| Be²⁺   | 402341    |
| B³⁺    | 41022     |
| C⁴⁺    | 59860     |
| N⁵⁺    | 402743    |
| Na⁺    | 401210    |
| Mg²⁺   | 411175    |
| Al³⁺   | 34475     |
| Si⁴⁺   | 34096     |
| P⁵⁺    | 415715    |
| S⁴⁺    | 14151     |
| S⁶⁺    | 14151     |
| K⁺     | 81528     |
| Ca²⁺   | 107304    |
| V³⁺    | 41060     |
| V⁵⁺    | 409501    |
| Cr³⁺   | 40205     |
| Cr⁵⁺   | 82360     |
| Cr⁶⁺   | 66097     |
| Mn²⁺   | 281280    |
| Mn³⁺   | 67888     |
| Mn⁵⁺   | 280693    |
| Fe²⁺   | 72389     |
| Fe³⁺   | 68523     |
| Co⁺    | 72387     |
| Rb⁺    | 81529     |
| Cu⁺    | 86066     |
| Zn²⁺   | 80376     |
| Ga³⁺   | 86016     |
| Se⁶⁺   | 108857    |
| Sr²⁺   | 71059     |
| Nb⁵⁺   | 412060    |
| Mo⁶⁺   | 409473    |
| Ag⁺    | 23111     |
| Cd²⁺   | 4097      |
| Cs⁺    | 72546     |
| Ba²⁺   | 71060     |
| La³⁺   | 411742    |
| Ce³⁺   | 402910    |
| Ce⁴⁺   | 74791     |
| Element | Isotopic Mass |
|---------|--------------|
| Pr$^{3+}$ | 72107        |
| Nd$^{3+}$ | 410848       |
| Sm$^{3+}$ | 240312       |
| Eu$^{2+}$ | 59257        |
| Er$^{3+}$ | 84706        |
| Yb$^{3+}$ | 59258        |
| Lu$^{3+}$ | 240311       |
| Hf$^{4+}$ | 97997        |
| Ta$^{5+}$ | 412585       |
| W$^{6+}$  | 409472       |
| Pb$^{2+}$ | 410915       |
### Table S2: A priori bond valences for crystal structures used in text

|          | K      | Cu     | Fe, C1-C3 | Σ   |
|----------|--------|--------|-----------|-----|
| N1       | 0.089  | 0.321  | 2.321     | 3   |
| N2       | 0.107  | 0.339  | 2.339     | 3   |
| N3       | 0.107  | 0.339  | 2.339     | 3   |
| Σ        | 1      | 2      | 14        |     |

|          | Hf     | Σ   |
|----------|--------|-----|
| N        | 0.5 × 8 | 3   |
| Σ        | 4      |     |

|          | Li1    | Li2   | Li3   | Ta   | Σ |
|----------|--------|-------|-------|------|---|
| N1       | 0.167  | 0.167 | 1.167 | 3    |
| N2       | 0.333  | 0.25  | 0.25  | 1.333| 3 |
| Σ        | 1      | 1     | 1     | 5    |

|          | Li     | Ba1   | Ba2   | Ba3   | Ba4   | Ba5   | M1    | M2    | Σ |
|----------|--------|-------|-------|-------|-------|-------|-------|-------|---|
| M* = W, Mo | LiBa4(M*2,N7) | Li | Ba1 | Ba2 | Ba3 | Ba4 | Ba5 | M1 | M2 | Σ |
| N1       | 0.268  | 0.316 | 0.315 | 0.299 | 1.535 | 3    |
| N2       | 0.268  | 0.317 | 0.315 | 0.212 | 1.573 | 3    |
| N3       | 0.099  | 0.083 | 0.196 | 1.557 | 3    |
| N4       | 0.331  | 0.379 | 0.362 | 1.597 | 3    |
| N5       | 0.249  | 0.252 | 0.301 | 1.338 | 3    |
| N6       | 0.280  | 0.283 | 0.331 | 0.227 | 1.550 | 3    |
| N7       | 0.082  | 0.080 | 0.170 | 1.338 | 3    |
| N8       | 0.223  | 0.274 | 0.273 | 0.176 | 1.531 | 3    |
| Σ        | 1      | 2     | 2     | 2     | 6    | 6    |
