The Structures of Ordered Defects in Thiocyanate Analogues of Prussian Blue

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File list (4)

BiSCN_defects_Chemrxiv.pdf (3.18 MiB)
BiSCN_defects_SI.pdf (519.45 KiB)
videos.zip (4.22 MiB)
structures_consolidated.zip (3.57 MiB)
The structures of ordered defects in thiocyanate analogues of Prussian Blue†

Matthew J. Cliffe,*a,b Evan N. Keyzer,a Andrew D. Bond,a Maxwell A. Astleb and Clare P. Greya

We report the structures of six new divalent transition metal hexathiocyanatobismuthate frameworks with the approximate formula $M^{II}[Bi(SCN)_6]_{1-x} \cdot xH_2O$, $M = Mn, Co, Ni$ and $Zn$. These frameworks are defective analogues of the perovskite-derived trivalent transition metal hexathiocyanatobismuthates $M^{III}[Bi(SCN)_6]$. The defects in these new thiocyanate frameworks order and produce complex superstructures due to the low symmetry of the parent structure, in contrast to the related and more well-studied cyanide Prussian Blue analogues. Despite the close similarities in the chemistries of these four transition metal cations, we find that each framework contains a different mechanism for accommodating the lowered transition metal charge, making use of some combination of $Bi(SCN)_3$ vacancies, $M_Bi$ antisite defects, water substitution for thiocyanate, adventitious extra-framework cations and reduced metal coordination number. These materials provide an unusually clear view of defects in molecular framework materials and their variety suggests that similar richness may be waiting to be uncovered in other hybrid perovskite frameworks.

1 Introduction

Defects are ubiquitous in functional materials and play a critical role in materials as simple as the binary rocksalt oxides1,2 and as complex as high-temperature superconductors3. The importance of vacancy chemistry to molecular framework perovskites is becoming increasingly clear4 in many important families, including the hybrid metal–halide semiconductors5,6, cyanide Prussian Blue analogue battery cathodes7,8 and magnetic formate perovskites9,10, as the number of studies making use of defect-engineering in these materials grows. Perhaps the most widespread strategy for introducing defects is aliovalent doping, where an ion is replaced by an ion with a different charge. Thus far, cationic dopants have been the most widely used and have been introduced onto both the $A$, e.g. $NH_3CH_2CH_2NH_2^+$ substitutes for $CH_3NH_3^+$ in $CH_3NH_3[MA]^+$ to produce ‘hollow’ perovskites,5 and the $B$ site, e.g. $Fe^{2+}$ substitutes for $Fe^{3+}$ in Prussian Blue11. In hybrid perovskites, these charged point defects are typically compensated by low-energy point defects of the opposite charge, most commonly vacancies, rather than by electronic defects.12 For example, in the ‘hollow’ lead

† Electronic Supplementary Information (ESI) available, which includes details of synthesis, single crystal and powder X-ray diffraction and videos of symmetry-mode decomposition of structures. See DOI: 10.1039/b000000x/

‡ Additional footnotes to the title and authors can be included e.g. ‘Present address’ or ‘These authors contributed equally to this work’ as above using the symbols: †, §, and ¶. Please place the appropriate symbol next to the author’s name and include a \footnotetext entry in the the correct place in the list.

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iodide perovskites, the additional A site charge is compensated primarily by vacancies on the B site, and can be represented in the Kröger-Vink defect notation by

\[ 2EN^{V_{MA}} + V^{β}_{Pb}. \] (1)

However, this simplified defect reaction only provides a partial description of the structure of these defective materials. Bulk chemical analysis indicates that in addition to B site vacancies ‘hollow’ perovskites contain a substantial concentration of iodide vacancies, as much as 6%, and diffraction measurements indicate the presence of local defect-ordering beyond that visible in the average structure.\(^5\) This example illustrates the general propensity for defective hybrid materials to contain both a wide diversity of point defects and for correlated defect disorder to emerge from the interactions between defects.

These two trends are just as important for the Prussian Blue analogue (PBA) family of cyanide frameworks. In Prussian Blue itself, the substitution of Fe\(^{III}\) for Fe\(^{II}\) is compensated by the formation of Fe(CN)\(_6\)^{4−} vacancies:

\[ 4Fe(II)Fe(III) + V_{Fe(III)(CN)6}^{β}. \] (2)

leading to a final composition Fe\(^{III}\)_4(Fe\(^{II}\)(CN))\(_6\)I\(_3\)·14H\(_2\)O.\(^{11}\) A second composition, M\(^{II}\)\(_2\)M[II]\(^{III}\)(CN)\(_6\)\(_2\)·xH\(_2\)O, containing M\(^{III}\)(CN)\(_6\)^{3−} vacancies also commonly occurs in PBAs.\(^{13}\) These hexacyanometallate vacancies produce large voids which are filled with water clusters in the as-synthesised materials.\(^{11,13}\) Both the vacancies and the water clusters play a critical role in determining the functional properties of these frameworks, including their mechanical robustness,\(^{14}\) their stability as pigments,\(^{15}\) and whether they show photomagnetism.\(^{16}\) In addition, the ordering in space of these defects will likely play a key role in mass transport through these materials for applications including ionic conduction and gas sorption.\(^{7,8,17,18}\)

PBAs also demonstrate one of the significant challenges of studying defective hybrid frameworks: it can be extremely difficult to determine their structures. Although dozens of compositions of PBAs have been reported,\(^{17}\) they are typically produced as microcrystalline powders, which inherently limits the amount of information available through diffraction.\(^{19}\) Even for single crystal and total scattering studies where information about the correlation of vacancies through the lattice can be obtained, the high symmetry of the parent structure means the local defect-structure determined through crystallography is superimposed on both the non-defective structure and the symmetry-related transformations of the defect, hindering detailed interpretation.\(^{8,13,20,21}\) The presence of disorder also complicates the interpretation of spectroscopic data, as deconvolution of different defect sites can often be challenging unless there are additional helpful features such as moderate paramagnetism.\(^{22}\) These problems are by no means unique to PBAs\(^9\) and thus, despite the utility of accurate representations of defect-structures, we are often forced to resort to simplified models which omit the true complexity of defective molecular frameworks.

There is now growing interest in the potential of thiocyanate analogues of PBAs as functional materials,\(^{23,24}\) and we have recently shown that hexathiocyanatobismuthamate can be a versatile building block for the formation of Prussian Blue/perovskite-type structures M[Bi(SCN)\(_6\)] (M = Sc\(^{3+}\), Cr\(^{3+}\), Fe\(^{3+}\)).\(^{25}\) The thiocyanate anion imparts strong optical absorption to the framework through ligand to metal charge transfer bands and also introduces large octahedral tilts through the bent Bi–S–C bond angle, thereby significantly reducing both the symmetry and volume of the frameworks.

In this paper we investigate the defect chemistry of thiocyanate analogues of Prussian Blues by investigating the divalent analogues with the approximate composition M\(_x\)[Bi(SCN)\(_6\)]. M=Mn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\) [Table 1], in part inspired by previous partial reports of other transition metal thiocyanates hexathiocyanatobismuthamates.\(^{26,27}\) This aliovalent substitution introduces a high concentration of defects which, when combined with the low symmetry of the parent structure, produces long-range defect order. The presence of long-range order allows us to carry out detailed crystallographic investigations of both the identities and distribution of defects. We find that despite the close similarities between the chemistry of these transition metals, the defect structures are diverse, in both local structure and long-range order. We show that the point defects in these frameworks include [Bi(SCN)\(_6\)]\(^{3−}\) vacancies, water clusters of up to 20 molecules, anti-site defects, and incorporation of interstitial charge-balancing cations. These point defects order into complex superlattice patterns which are, to the best of our knowledge, unknown in perovskites, both hybrid and conventional. We also find that where lower coordination-numbers are feasible for the transition metal, e.g. Zn\(^{2+}\), new ordered structures can be favoured over defective frameworks. The range of chemistry found in these materials suggests that control over defects could produce surprising new chemical functionality throughout molecular perovskites.

### Table 1 Summary of reported compounds

| Formula                  | \(\text{V}_{\text{Bi(SCN)}}\)(\(\text{NCS})_2\)\_Bi | \(\text{V}_{\text{Bi(SCN)}}\)(\(\text{NCS})\_Bi | \(\text{V}_{\text{Bi(SCN)}}\)\(\text{Bi})_\text{Bi} | \(\text{V}_{\text{Bi(SCN)}}\)(\(\text{NCS})\_Bi | \(\text{V}_{\text{Bi(SCN)}}\)(\(\text{NCS})\_Bi | \(\text{V}_{\text{Bi(SCN)}}\)(\(\text{NCS})\_Bi |
|-------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| \(\text{Mn}_2\text{Bi}(\text{SCN})_7\cdot7\text{H}_2\text{O}\) | \(\text{Mn}_2\text{Bi}(\text{SCN})_7\cdot7\text{H}_2\text{O}\) | \(\text{Mn}_2\text{Bi}(\text{SCN})_7\cdot7\text{H}_2\text{O}\) | \(\text{Mn}_2\text{Bi}(\text{SCN})_7\cdot7\text{H}_2\text{O}\) | \(\text{Mn}_2\text{Bi}(\text{SCN})_7\cdot7\text{H}_2\text{O}\) | \(\text{Mn}_2\text{Bi}(\text{SCN})_7\cdot7\text{H}_2\text{O}\) | \(\text{Mn}_2\text{Bi}(\text{SCN})_7\cdot7\text{H}_2\text{O}\) |
| \(\text{Co}_5\text{Bi}_6(\text{SCN})_3\cdot(\text{H}_2\text{O})_\text{Bi} | \(\text{Co}_5\text{Bi}_6(\text{SCN})_3\cdot(\text{H}_2\text{O})_\text{Bi} | \(\text{Co}_5\text{Bi}_6(\text{SCN})_3\cdot(\text{H}_2\text{O})_\text{Bi} | \(\text{Co}_5\text{Bi}_6(\text{SCN})_3\cdot(\text{H}_2\text{O})_\text{Bi} | \(\text{Co}_5\text{Bi}_6(\text{SCN})_3\cdot(\text{H}_2\text{O})_\text{Bi} | \(\text{Co}_5\text{Bi}_6(\text{SCN})_3\cdot(\text{H}_2\text{O})_\text{Bi} | \(\text{Co}_5\text{Bi}_6(\text{SCN})_3\cdot(\text{H}_2\text{O})_\text{Bi} |
 vacancies are occupied by molecular aqua-Mn(II) thiocyanate complexes with average composition Mn(H$_2$O)$_3$(NCS)$^+$, connected to the framework by hydrogen bonds [Fig. 2(b)]. The positive charge on the molecular complex is balanced to the framework by a long range ordered and lie within every third (010) layer of metal atoms, corresponding to a {110}-type layer in the primitive cubic BX$_3$ aristotype. Within these (010) planes, all the Bi(SCN)$_6^{3-}$ are missing, so that the structure comprises two successive non-defective layers followed by a third defective layer containing only Mn metal ions [Fig. 3]. This defect ordering pattern lowers the symmetry of the cubic aristotype to the orthorhombic Immm space group. When combined with the cooperative octahedral tilts produced by the bent M-SCN bonding, the structure lowers to the observed P2$_1$/n space group. We confirmed that the observed framework structure is related to the parent structure within the descent-of-symmetry framework by using the ISODISTORT software package and Topas Academic.

[ESI Video 1]. They are therefore be alternatively written as Mn[Bi(SCN)$_6$]$_{1-x}$·xNCS·x[Mn(H$_2$O)$_3$(NCS)]·9.4(H$_2$O), $x = \frac{1}{2}$. The molecular Mn(II) complex is disordered and the charge-balancing thiocyanate are disordered, with the site bound to the metal atom with literature values confirms that all framework transition parameters. The complexity of the network means that the site bonded to the molecular Mn(II) complex showing the reverse. When the temperature of the crystal was raised to 300 K this ratio was found to be instead 0.7:0.3, indicating that a higher proportion of the NCS ligands are now bound to the framework. Using an analogous route to the synthesis of 1 but substituting basic cobalt carbonate for manganese carbonate, we were able to synthesize a new framework of composition Co$_3$Bi$_6$(NCS)$_{36}$(H$_2$O)$_{38}$ (2). Compound 2 also has a defective Prussian Blue structure with missing hexathiocyanatoisothionate anions, however the mechanism by which this is accommodated is quite distinct from that of 1. In 2 Bi(SCN)$_6$ vacancies order into alternate (001) layers, within which half of all Bi(SCN)$_6$ polyhedra are absent in a chequerboard fashion. This gives a total vacancy concentration of $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$ [Fig. 4c]. The vacant sites are then filled by large 18 molecule water clusters in one half of the (001) layers and in the other half by charge balancing hydrated metal cations, Co(H$_2$O)$_6^{2+}$·14H$_2$O cations [Fig. 4(a,b)]. The chemical formula can be therefore be alternatively written as Co[Co(SCN)$_6$]$_{1-x}$·$\frac{x}{2}$Co(H$_2$O)$_6$(H$_2$O)$_{14}$·$\frac{x}{2}$(H$_2$O)$_{18}$, $x = \frac{1}{4}$.

Significant disorder is present for both the H$_2$O$_{18}$ and Co(H$_2$O)$_6^{2+}$·14H$_2$O clusters, which prevents the determination of the hydrogen atom positions due to the large atomic displacement parameters. The complexity of the network means that the exact hydrogen bonding pattern remains unknown, though it is clear from the distances between O atoms and their geometric arrangement that significant hydrogen bonding is present. Six waters in each cluster coordinate to the framework Co(II) atoms, completing the octahedral coordination environment of the metal atoms. Comparison of the bond valence sums of each of the Co atoms with literature values confirms that all framework transi-

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**Fig. 2** (a) Crystal structure of Mn$_2$[Bi(SCN)$_6$](NCS)·7H$_2$O (1) at 300K. A dashed ellipse highlights the manganese molecular complex, shown in greater detail in (b). Disorder around the molecular cluster has been omitted in both (a) and (b) to aid visualisation. (c) A close-up view of the octahedral tilts produced by the bent M-SCN bonding, the structure lowers to the observed P2$_1$/n space group. We confirmed that the observed framework structure is related to the parent structure within the descent-of-symmetry framework by using the ISODISTORT software package and Topas Academic.

**Fig. 3** Defect ordering pattern for 1. (a) A view along the a axis. (b) A slice through the ab-plane, with $c \approx \frac{1}{2}$
tion metal atoms remain in the Co(II) oxidation state. The hexa-aquacobalt complex which occupies half the Bi vacancy sites has very enlarged atomic displacement parameters and significantly lengthened Co-O bond lengths compared to similar complexes. Elemental analysis (energy-dispersive X-ray spectroscopy on crystalline samples and ICP-OES on the framework dissolved in HNO$_3$) confirmed the absence of other adventitious cations such as Ca$^{2+}$ and refinement of the structure with hexaquacobalt produced a significantly worse quality of fit to the experimental diffraction data. As the refined structure show no other defects and in the absence of other plausible candidates, we therefore believe this cation is likely to be Co(II).

The observed defect ordering would, on its own, reduce the symmetry of the primitive cubic aristotype to a $2 \times 2 \times 2$ $I4/mmm$ structure, and when combined with octahedral tilting, this yields the resultant $2 \times 2 \times 2$ $P\bar{T}$ symmetry [ESI Video 2]. This structure relates to the M[Bi(SCN)$_6$] structure through the following transformation matrix:

$$
\begin{pmatrix}
  a' \\
  b' \\
  c'
\end{pmatrix} =
\begin{pmatrix}
  1 & -1 & 0 \\
  1 & 1 & 0 \\
  0 & 0 & 2
\end{pmatrix}
\begin{pmatrix}
  a \\
  b \\
  c
\end{pmatrix}.
$$

2.3 Compounds 3 and 4: M$_6$Bi$_5$(SCN)$_{30}$·3NH$_4$, M = Co & Ni

We also explored the synthesis of frameworks using NH$_4$SCN. We found that by using NH$_4$SCN as a source of SCN$^-$ and reacting it with Co(NO$_3$)$_2$ and Bi(NO$_3$)$_3$ using dilute HNO$_3$ as a solvent, small, diffraction quality single crystals of a new phase, Co$_6$Bi$_5$(SCN)$_{30}$·16H$_2$O·3NH$_4$ (3), formed rapidly, which incorporates NH$_4$ cations. Whereas our attempts to synthesise Ni-based frameworks using HSCN and basic Ni salts failed, we were able to use this new route to produce a new framework isostructural to 3, Ni$_6$Bi$_5$(SCN)$_{30}$·16H$_2$O·3NH$_4$ (4). Single crystal diffraction revealed that 3 and 4 are defective perovskite frameworks containing Bi(SCN)$_6^{3-}$ vacancies, the structures of which can be thought of, like 2, as (100) perovskite blocks separated by vacancy containing layers. Just as in 2, these Bi(SCN)$_6^{3-}$ vacancies order in a chequerboard fashion in (100) layers, however, only every third layer contains vacancies and so the total vacancy concentration is $\frac{1}{3}$. The formula can therefore be alternatively written as Co[Bi(SCN)$_6$]$\cdot$$\frac{x}{3}$[16H$_2$O·3NH$_4$]·2x(NH$_4$)$_3$, $x = \frac{1}{6}$.

These vacancies compensate for half the negative charge introduced by substituting M(II) for M(III). The remaining charge is compensated by interstitial ammonium cations, which occupy two different sites, the first between two non-defective layers, and the second as part of the large 18 atom water cluster. This water cluster, like that in 2, shows significant disorder, in part because each cluster lies across a centre of symmetry but contains only one NH$_4^+$ cation. The presence of the NH$_4^+$ cation was inferred from charge balance constraints, and which of the electron density peaks was NH$_4^+$ was decided on the basis of two factors: as it is half-occupied it will be the source of the disorder and it will be a better hydrogen bond donor than other water atoms. As we were unable to locate the H-atoms, definitive assignment to the M[Bi(SCN)$_6$] phases we describe,

$$
\begin{pmatrix}
  a' \\
  b' \\
  c'
\end{pmatrix} =
\begin{pmatrix}
  1 & 1 & 0 \\
 -1 & 1 & 0 \\
 -\frac{1}{2} & 0 & \frac{1}{2}
\end{pmatrix}
\begin{pmatrix}
  a \\
  b \\
  c
\end{pmatrix}.
$$

2.4 Compounds 5 and 6: Zn$_2$[Bi(SCN)$_6$]$_2$

Addition of Zn(NO$_3$)$_2$ to a dilute HNO$_3$ solution of H$_3$[Bi(SCN)$_6$]$_3$ prepared from NH$_4$SCN produced single crystals over a period of minutes, and by single crystal X-ray diffraction we were able to solve two distinct polymorphic frameworks, $\alpha$–Zn$_2$[Bi(SCN)$_6$]$_2$ (5) and $\beta$–Zn$_2$[Bi(SCN)$_6$]$_2$ (6) [Fig. 6]. Despite the similarity in synthesis route to that used for 3 and 4, these new phases do not incorporate NH$_4$ from solution. In addition, unlike the other phases we describe, 5 and 6 do not contain lattice water and their
structures are much less closely related to that of Fe[Bi(SCN)]$_6$.

Rietveld refinement of a polycrystalline sample confirmed that the polymorphs crystallise concomitantly, with the predominant fraction consisting of the $\beta$ phase (92%) [ESI Fig. 1].

Careful examination of the powder X-ray diffraction data showed that the product contains at least one additional phase which we have been unable to isolate. As with the Prussian-Blue derived frameworks, the bent NCS–Bi bond angle leads to the formation of low symmetry structures, with multiple symmetry distinct metal sites in each (in $\alpha$, two Bi and two Zn sites, and in $\beta$ two Bi and three Zn sites).

The local connectivity is identical between the two phases, and there are only minor differences in bond lengths and angles. Despite these similarities, the topologies of framework connectivity of the $\alpha$ and $\beta$ phases are very different. Indeed, by using the ToposPro software, we were able to determine that the graphs produced by considering the Zn$_3$Bi$_2$ sublattice for both $\alpha$ and $\beta$–Zn$_3$Bi$_2$(SCN)$_6$ possess topologies which were not yet recorded in the ToposPro topology database. We have termed these new topologies clw1, point symbol: $\{4^3,6^3\}2\{4^4,6^0,8^1\}\{4^4,6^2\}\{4^6,6^0,8^1\}$ and clw2, point symbol: $\{4^2,6^1\}\{4^3,6^3\}\{4^4,6^1\}\{4^4,6^2\}\{4^5,6^3,8\}$.

The $\alpha$ phase is derived from the parent phase by the incorporation of Zn$^{2+}$ interstitials in half of all layers. More completely, it is built from two different layers, a Prussian Blue-like layer and CdI$_2$-like layer, which stack in an alternating fashion along the $a$ axis to form a three-dimensional framework [Fig. 6(d)].

The Prussian Blue-like layer has the composition ZnBi(SCN)$_4$ and can be described as a {100} layer of a hypothetical `ZnBi(SCN)$_6$' analogue of the Fe[Bi(SCN)$_6$] structure [Fig. 6(e)]. As the Zn is four-coordinated, its bonding requirements are satisfied within the layer, and so the layer is connected to the layers above and below through the Bi atom. The second layer has composition Zn$_3$Bi(NCS)$_6$. NCS and a pseudo-CdI$_2$ structure, where the Bi (‘Cd’) atoms approximately form a triangular lattice, in which the interstices are occupied by Zn (‘I’) atoms [Fig. 6(f)]. In this layer, the Bi atoms are saturated by bonds within the layer, and so the connection to the other layer occurs through the Zn atoms, which are bound to an additional thiocyanate.

The predominant size of ring in the $\beta$–Zn$_3$Bi$_2$(NCS)$_6$ phase is the sixteen-membered Zn$_2$Bi$_2$(NCS)$_4$ ring (four-membered ring, considering only metal cations) common to the M[Bi(SCN)$_6$] perovskite. The ring–statistics are otherwise very different [Fig. 6(e)] and the structure cannot be easily decomposed into simple crystal-chemical units. The coordination geometry for both $\alpha$ and $\beta$ phases remain similar, and there is only slightly larger variation in the octahedral coordination of BiS$_6$ distortions in the $\beta$ phase.

The differences observed between Zn-based frameworks and the other transition metals derives from the increased favourability of the tetrahedral coordination, which permits the formation of charge-neutral and coordinatively saturated frameworks from Zn(NCS)$_4$ tetrahedra and Bi(SCN)$_6$ octahedra without the need for point vacancies or coordinating water molecules. This is directly akin to the cyanide Prussian Blue family, for which Zn$_3$[Fe(CN)$_6$]$_2$ can form both an ordered phase in which zinc is tetrahedrally coordinated, and a defective disordered cubic phase, analogous to the other Prussian Blues, in which Zn is octahedrally coordinated. In Zn$_3$[Fe(CN)$_6$]$_2$, the polymorphism occurs between a disordered and an ordered phase, whereas both polymorphs of Zn$_3$[Bi(SCN)$_6$]$_2$ are ordered.
3 Discussion

To the best of our knowledge, the only previous reports of any compounds belonging to this family were by Cyganek,26,27 but in these early studies the analysis was confined principally to determining their composition. The following compositions were reported: MnBi(SCN)₃, Mn₃[Bi(SCN)]₆₂⁻·7H₂O, Mn₂[Bi(SCN)]₆₋₁.²·12H₂O, Ni₃[Bi(SCN)]₆₋₂·10H₂O, which do not correspond to any of the phases uncovered in our study; Co₃[Bi(SCN)]₆₋₂·12H₂O which corresponds approximately to 2, and Zn₃[Bi(SCN)]₆₋₋ which corresponds to 5 and 6. The fact that these early studies report compositions we have not yet synthesised ourselves indicates that perhaps there is even more latent complexity in this family of materials than we have uncovered.

Aside from 6, all structures retain strong similarities to the parent Fe[Bi(SCN)]₆ structure, despite the stark differences in composition. If one normalises the cell volume by the number of Bi atoms, this normalised volume is within a few percent of Fe[Bi(SCN)]₆ for every compound, with the biggest discrepancy (5.5%) found for compound 6. This suggests that the high vacancy concentration does not produce significantly contracted frameworks, which is likely due to the fact that potential voids are filled by water clusters and molecular complexes. For the compounds containing octahedrally coordinated transition metal ions, 1–4, the pattern of tilts observed in the parent structure is retained [ESI Videos 1–3]. In addition, the (large) magnitude of the octahedral tilting is not significantly perturbed, as the primary source of tilts is the shape of the frontier orbitals of NCS⁻ and the resultant bent Bi-S-C bond angle. The retention of tilt-cooperativity in each of 1–4 is more surprising and is probably due in part to the presence of three dimensional connectivity of octahedra combined with the fact that no framework node has lower than four-fold coordination. These factors suggest that this Fe[Bi(SCN)]₆ structure type is robust and likely to be found in other members of this family, and is suggestive that porous analogues may well be possible.

The introduction of a divalent metal such as Mn²⁺ onto a trivalent metal site, M, introduces a single net negative charge, in the Kröger-Vink notation, MnM⁻. As the framework is an overall charge-neutral neutral the framework must compensate by introducing charge balancing defects, and we found that there are a wide variety of mechanisms. α-Zn₃[Bi(SCN)]₆⁻ can be thought of as containing Zn³⁺ interstitials:

\[ 2ZnM⁺ + Zn⁻ \]  

(7)

For the other transition metals, the transition metals retain octahedral coordination, even though tetrahedral Co(II) is well-known, and so they adopt structures more closely related to the M[Bi(SCN)]₆ structure. Compounds 1–4 all contain Bi(NCS)₃⁻ vacancies, and a key difference in these structures is how the resultant voids are filled and the open structures are stabilised. This is also a feature of the cyanide Prussian Blues, which contain significant quantities of zeolitic water.33 These thiocyanate frameworks have more complex structures than reported for PBAs, although similar complexity may be present in cyanide compounds but be more difficult to detect due to their higher symmetries.

Compound 1, contains molecular Mn(NCS)₂(H₂O)₄ complexes in the V₁₂(BiSCN)₆ sites which are hydrogen-bonded to the network, instead of water clusters, summarised as:

\[ 3MnM⁺ + [Mn(NCS)]₂[Bi(SCN)]₆⁻ \]  

(8)

Compound 2, like 1, contains anti-site type transition metal cations, which occupy half the V₁₂(BiSCN)₆ sites. However, these Co³⁺ cations are not coordinated to thiocyanates, and water clusters occupy the remaining half of V₁₂(BiSCN)₆ sites, that is:

\[ 8CoM⁺ + V₁₂(BiSCN)₆⁻ + Co[Bi(SCN)]₆⁻ \]  

(9)

The presence of other interstitial cations, such as NH₄⁺ in 3 and 4, adds an additional avenue for complexity, just as found in the cyanide Prussian Blues. Both 3 and 4 compensate for the effective negative charge of the divalent cation by the formation of V₁₂(BiSCN)₆, which are all filled with water clusters, and ammonium cations:

\[ 6NiM⁺ + V₁₂(BiSCN)₆⁻ + 3(NH₄)⁺ \]  

(10)

The ability of the thiocyanate perovskite framework to accommodate monovalent A-site cations has been previously demonstrated for CsCd(NCS)₃ and (NH₄)₂CdNi(NCS)₆.

4 Conclusion

We have found six new framework compounds of the approximate formula Mᴵ[Bi(SCN)]₆₋₋. The primary mechanism by which the charge of aliovalent M(II) cations is accommodated by the frameworks is through the introduction of Bi(SCN)₆ vacancies, analogous to the M(CN)₆ vacancies found in the Prussian Blue; however anti-site defects, large water clusters and even neutral molecular metal complexes are also accommodated. In addition to this, we find that the low symmetry of the structure enables long-range order of these defects: we find that vacancies tend to segregate into {100} or {110} type layers. The complexity of these structures is such that single-crystal X-ray diffraction data is necessary to uncover it.

Despite the relatively high concentration of vacancies, we also found that the octahedral tilt patterns of the pattern structures are retained in all the Prussian Blue-derived members of this family, showing their robust nature. Compounds 3 and 4 demonstrate that as in the Prussian Blues, the presence of other cations can have a powerful effect on the resultant structure, as their incorporation leads to drastically different ordering patterns. In conclusion, we have shed light on the surprising complexity of aliovalent doping in this family of hybrid framework materials. We anticipate that as the investigation of hybrid frameworks advances, the range of defects we have uncovered in thiocyanate frameworks will be reflected in other anion chemistries. These novel defect types will have different energetic formation costs, and the complex orderings will perturb the cooperative properties, such as mechanical flexibility and magnetism. The adaptability of these structures further suggests that guests of significant complexity, including molecular complexes, could be included in these frameworks, whether directly in synthesis or post-synthetically through ion-exchange processes.
5 Conflicts of Interest
There are no conflicts of interest to declare.

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The structures of ordered defects in thiocyanate Prussian Blue analogues

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1 Synthetic Procedures

The synthesis procedures were adapted from those reported in S1.

1.1 Synthesis of HSCN

In a 250 mL round bottom flask, NH₄SCN (5g, 65.7 mmol) was dissolved in 5 mL H₂O and cooled to 0 °C in an ice bath. A H₂SO₄ solution (ca. 7 ml of H₂SO₄ in 12 ml H₂O) was then added dropwise to the cooled NH₄SCN solution. The reaction mixture was stirred for 30 mins before being warmed to room temperature. The aqueous mixture was subsequently extracted with diethyl ether (2 × 20 ml) and the organic phase was retrieved and its volume reduced by half using a stream of N₂.

1.2 Synthesis of H₃[Bi(SCN)₆] solution

Bi₂O₂(CO₃) (0.50 g, 0.98 mmol) was suspended in ca. 12 mL H₂O followed by the addition of the HSCN/ether solution. The resulting reaction mixture was stirred vigorously under a slight flow of N₂ until all ether had been removed and the solution had turned bright orange. Any remaining solids were filtered off and the orange solution was placed under a slight vacuum to remove any excess HSCN.

1.3 Synthesis of 1

1mL of the prepared H₃[Bi(SCN)₆] was added to approximately 50 mg MnCO₃, and left to react overnight. Any excess solids were removed by gravity filtration. The dark red solution was then left to evaporate in a watch glass covered by petri-dish for a period of approximate two weeks until diffraction quality dark orange single crystals formed.

1.4 Synthesis of 2

1mL of the prepared H₃[Bi(SCN)₆] was added to approximately 50 mg (Co₅(CO₃)₂(OH)₆) and left to react overnight. Any excess solids were removed by gravity filtration. The dark red solution was then left to evaporate in a watch glass covered by petri-dish for a period of approximate two weeks until diffraction quality dark orange single crystals formed.

1.5 Synthesis of 3 and 4

Bi(NO₃)₃ · 2.5 H₂O (3 mmol, 1.46 g) was dissolved in 1.5 mL 3M HNO₃, and a solution of NH₄SCN (13.1 mmol, 1.00 g) dissolved in 2 mL of distilled water was added to it, producing a vivid orange solution. Ni(NO₃)₂ · 6 H₂O (7 mmol, 2.036 g) was dissolved in 2 mL of water and then added to to bismuth thiocyanate solution, which on standing produced numerous small very dark orange single crystals of 4 over a period of 15 min. The same route can be used to produce 3, substituting Co(NO₃) · 6 H₂O.

1.6 Synthesis of 5 and 6

Bi(NO₃)₃ · 2.5 H₂O (3 mmol, 1.46 g) was dissolved in 1.5 mL 3M HNO₃, and a solution of NH₄SCN (13.1 mmol, 1.00 g) dissolved in 2 mL of distilled water was added to it, producing a vivid orange solution. Zn(NO₃)₂ · 6 H₂O (7 mmol, 2.082 g) was dissolved in 2 mL of water and then added to to bismuth thiocyanate solution, which on standing produced an immediate precipitate of numerous orange single crystals of 5 and 6.
2 Single Crystal X-ray Diffraction

Single crystals were selected and mounted using perfluorinated oil on a polymer-tipped micromount and cooled rapidly to measurement temperature 120 K or 180 K in a stream of cold N\textsubscript{2} using an Oxford Cryosystems open flow cryostat. To enable variable temperature measurements, the crystal used for structures 1 and 1a was mounted using varnish on a pin.

Single-crystal X-ray diffraction data for 2, 4, 5 and 6 were collected using a Nonius KappaCCD diffractometer, using graphite monochromated MoK\textsubscript{α} radiation ($\lambda = 0.7107$ Å). Data for 1 and 1a were collected using a Bruker D8-Quest PHOTON-100 diffractometer equipped with an Incoatec I\textsubscript{µ}S Cu microsource ($\lambda = 1.54056$ Å). Data for 3 were collected using Single crystal X-ray diffraction data were collected on an Oxford Diffraction GV1000 (AtlasS2 CCD area detector, mirror-monochromated Cu-K\textsubscript{α} radiation source ($\lambda = 1.54184$ Å). Structure solution was carried out using SHELXT and refinement with SHELXL, within the OLEX2 graphical interface.\textsuperscript{2–4} For crystal 1, hydrogen atoms were refined with constrained geometries and riding thermal parameters, however the disorder present in samples 2–4 meant that hydrogen atoms could not be located, aside from an NH\textsubscript{+} cation in 4. Disordered sites in structures 1, 2, 3 and 4 were modelled at half occupancy.
### ESI Table 1: Summary of key crystallographic parameters for all compounds

| Compound | 1 | 1a | 2 | 3 | 4 | 5 | 6 |
|----------|---|----|---|---|---|---|---|
| Formula  | Mn$_2$Bi(SCN)$_7$·7H$_2$O | Mn$_2$Bi(SCN)$_7$·7H$_2$O | Co$_5$Bi$_6$(SCN)$_3$6·(H$_2$O)$_3$8 | Co$_5$Bi$_6$(SCN)$_3$6·(H$_2$O)$_3$8 | Ni$_6$Bi$_6$(SCN)$_3$6·3NH$_4$·16H$_2$O | Ni$_6$Bi$_6$(SCN)$_3$6·3NH$_4$·16H$_2$O | α-Zn$_3$Bi$_2$(SCN)$_12$ | β-Zn$_3$Bi$_2$(SCN)$_12$ |
| Molar mass | 851.54 | 851.54 | 4535.47 | 4535.47 | 3438.91 | 3512.13 | 3438.91 | 3512.13 |
| Crystal System | Monoclinic | Monoclinic | Triclinic | Triclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space Group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $C2/c$ | $P2_1/c$ |
| Crystal Colour | dark orange | dark orange | dark orange | orange | dark orange | dark orange | orange | orange |
| $Z$ | 4 | 4 | 1 | 1 | 4 | 4 | 4 | 4 |
| Radiation | Cu K$_\alpha$ | Cu K$_\alpha$ | Mo K$_\alpha$ | Mo K$_\alpha$ | Cu K$_\alpha$ | Cu K$_\alpha$ | Mo K$_\alpha$ | Mo K$_\alpha$ |
| Temperature (K) | 300 | 180 | 180 | 180 | 180 | 111 | 111 | 111 |
| $a$ (Å) | 8.3698(3) | 8.3065(2) | 12.0209 (2) | 12.0209 (2) | 11.9106 (3) | 11.8567 (2) | 12.6310 (4) | 12.6310 (4) |
| $b$ (Å) | 26.0037(9) | 25.8428(6) | 12.1613 (2) | 12.1613 (2) | 11.9382 (3) | 11.8653 (2) | 18.3824 (4) | 18.3824 (4) |
| $c$ (Å) | 12.2466(4) | 12.2664(3) | 23.8319 (4) | 23.8319 (4) | 12.4250 (5) | 12.3824 (4) | 15.7403 (3) | 15.7403 (3) |
| $\alpha$ (Å) | 90 | 90 | 94.200 (1) | 94.200 (1) | 83.935 (2) | 84.0731 (7) | 90 | 90 |
| $\beta$ (Å) | 91.208(2) | 90.2360(10) | 94.003 (1) | 94.003 (1) | 76.504 (2) | 76.7140 (7) | 90 | 90 |
| $\gamma$ (Å) | 90 | 90 | 91.452 (1) | 91.452 (1) | 85.384 (2) | 85.1942 (8) | 90 | 90 |
| $V$ (Å$^3$) | 2664.83(16) | 2633.12(11) | 3464.52 (10) | 3464.52 (10) | 2652.04 (12) | 2498.60 (8) | 3496.00 (9) | 3496.00 (9) |
| Measured reflections | 30850 | 33300 | 21789 | 21789 | 37154 | 20614 | 7507 | 7507 |
| Independent reflections | 4712 | 4657 | 15385 | 15385 | 9921 | 11356 | 3975 | 3975 |
| $R_{int}$ | 0.1315 | 0.080 | 0.135 | 0.135 | 0.135 | 0.080 | 0.135 | 0.135 |
| $R(F^2 > 2\sigma(F^2))$ | 0.053 | 0.038 | 0.059 | 0.059 | 0.053 | 0.038 | 0.059 | 0.059 |
| $S$ | 1.03 | 1.03 | 1.13 | 1.13 | 1.03 | 1.03 | 1.13 | 1.13 |
| CCDC number |  |  |  |  |  |  |  |  |

Cu K$_\alpha$, $\lambda = 1.54056$Å, Mo K$_\alpha$, $\lambda = 0.71073$Å.
3 Powder X-ray Diffraction

A high-resolution synchrotron X-ray powder diffraction measurement on a ground powder of \( \text{Zn}_3\text{Bi}_2(\text{NCS})_{12} \) was carried out at beamline 11-BM at the Advanced Photon Source (APS) using a wavelength of 0.414537 Å. The sample was loaded into a 0.8 mm diameter Kapton capillary. Rietveld refinement of the data was carried out using Topas Academic 4.1. Lattice parameters were allowed to refine freely along with isotropic displacement parameters for Bi atoms and terms accounting for crystallite size broadening and crystallographic strain. The presence of a minor tertiary phase was modelled using independently refining peaks, which we were unable to index as a separate phase.

![Graph](image)

ESI Fig. 1: Rietveld refinement of mixed phase \( \alpha \) - and \( \beta \) \( \text{Zn}_3\text{Bi}_2(\text{SCN})_{6} \). * indicates the presence of an impurity peak.
4 ICP-OES

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was recorded on a Perkin Elmer, Optima 2000 DV ICP-OES with S10 autosampler. Samples and standards were prepared with a final solution composition of 2% nitric acid. Metal content was kept below 50 mg/L for ICP measurements as at higher concentrations a precipitate would form which would not dissolve in limited volumes of acids. Found for sample 2 Bi 27.35%, Co 17.97%, Ca 0.0%, Ni 0.0% and Ti 0.0%.

5 STEM-EDX

Energy dispersive X-ray (EDX) spectroscopy was acquired using dark field scanning transmission electron microscopy (STEM), performed using a JEOL JEM-2100+ microscope operated at 200 kV and an Oxford Instruments XMaxN 100TLE X-ray microanalysis system. Samples were deposited onto copper grid mounted “lacey” carbon films (Agar) and the beam was condensed to areas suspended over holes of the amorphous carbon to negate the contribution to the carbon signal from the support film. Copper contributions from the grid were discounted from the analysis. The measured proportions of light atoms (C, N and O) will have contributions from the carbon film and as these measurements were carried out under high vacuum, it is likely a significant proportion of lattice water will have been lost.

| Element | Wt%  | At%  | At. Ratio | At. Ratio (calc.) |
|---------|------|------|-----------|------------------|
| Bi      | 19.87| 2.02 | 2         | 2                |
| Co      | 9.74 | 3.51 | 3.47      | 3                |
| S       | 20.14| 13.32| 13.19     | 12               |
| C       | 23.9 | 42.18| 41.76     | 12               |
| N       | 21.61| 32.71| 33.39     | 12               |
| O       | 4.72 | 6.25 | 6.19      | 12.67            |
| Ca      | 0.02 | 0.01 | 0.01      | 0                |
| Ti      | 0    | 0    | 0         | 0                |
| Ni      | 0    | 0    | 0         | 0                |
ESI Fig. 2: Representative EDX spectrum for compound 2
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