Inorganic Metal Thiocyanates

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Metal thiocyanates are some of the earliest reported molecular framework materials and adopt a diverse range of structures. This review describes the structures, properties and syntheses of the known binary and ternary thiocyanates. It provides a categorization of their diverse structures, and connects them to the structures of atomic inorganic materials. In addition to this description of characterized binary and ternary thiocyanates, the review summarizes the state of knowledge for all other binary metal thiocyanates. The review concludes by highlighting opportunities for future materials development.

1 Introduction

Thiocyanate is one of the prototypical pseudohalide anions and it can be found in every area of contemporary chemistry, most commonly as a ligand in molecular metallocomplexes, but also as an organic functional group, in biological chemistry as a key metabolite with potential anticarcinogenic function, and even in space. The study of thiocyanate has a long history. NCS− was first prepared and isolated by Porrett in 1814, well before the isolation of elemental bromine, fluorine and iodine. In this pioneering work, Porrett used HNCS to prepare ‘sulferetted chyrazate’ salts of a number of elements, including K, Na, Ca, Al, Ba, Sr, Ag, Hg, Cu, Pb, Sn, Bi, Mn, Zn, Co, Ni, Pd, U, Mo and Cr. Porrett’s work highlights not only the diversity of thiocyanate chemistry but also how much is yet to be determined about metal thiocyanate chemistry: although these compounds were reported more than two hundred years ago, the synthesis and structures of Pd, U, Mo and Cr thiocyanate have not been confirmed. The presence of these open questions contrasts with the ‘true’ metal halides where nearly every feasible composition has been structurally characterized, from extreme oxidation states (e.g. VCl5) to highly radioactive compounds (e.g. EsCl3). Pseudohalides thus offer synthetic inorganic chemists the rare opportunity to create new (pseudo-)binary compounds (Fig. 1).

In this review, I describe what is known about the solid-state chemistry of inorganic metal thiocyanates. It presents a systematic overview of their structures and highlights opportunities for developing their chemistry further. The very extensive chemistry of thiocyanate in solution or with co-ligands has been excluded as it is well-covered elsewhere. The review summarizes the chemistry of the binary M(NCS)x for every non-radioactive metal, and the structure of every ternary metal thiocyanate MM(NCS)x. Special attention has been paid to the structural analogies between metal thiocyanates and other inorganic solid-state compounds. I have relied, in addition to the primary literature, on two book chapters: Golub, Köhler and Skopenko (1986) and Williams (1948) which are the most comprehensive summaries of metal thiocyanate chemistry thus far published. The review begins with a general overview of metal thiocyanates highlighting characteristic trends. It then moves onto a description of the chemistry of binary metal thiocyanates, describing first the five structural families before summarising what is known about the binary metal thiocyanates without reported crystal structures. The structures of the ternary metal thiocyanates are then described, being classified first by framework dimensionality and then by characteristic structural features. The review concludes with a brief summary and prospectus of the potential of inorganic metal thiocyanate chemistry.

1.1 Structural chemistry

Thiocyanate is a rigid linear anion. The key contrasts in the structural chemistry between the atomic halides anion and linear thiocyanate arise therefore from the additional degrees of freedom introduced by moving from a sphere to a rod. The most important new degree of freedom is the orientation of the NCS− ligand. This can be parameterized by the M-N-C and M-S-C angles for a bridging thiocyanate ligand. As thiocyanate is stiff, the intramolecular degrees of freedom are less important, and deviations from linearity and variations in the bond lengths (despite the two distinct resonance structures) are typically small. The orientation of NCS− is so important for the chemistry of thiocyanate because of the different bonding preferences of the N−.
and S-termini: the N-terminus is harder and typically coordinates well to harder first row transition metals and s-block metals; the S-terminus is softer, and most often coordinates to soft metals (late transition metals, 4d-, 5d-transition metals and late p-block metals). This asymmetry means that binary thiocyanates are harder to form than might otherwise be expected, because often thiocyanate will readily coordinate through one terminus (N-or S-) to a given metal but only bind weakly through the other end, meaning other ligands (including solvents such as water) can bind more strongly than thiocyanate itself. A common challenge in the synthesis of binary thiocyanates is therefore removing or avoiding competing ligands and coordinating solvents. The large chemical differences between N and S do offer opportunities for ternary phases however, and this has been exploited in the synthesis of cation-ordered ternary frameworks (see Section 2.3). A wide variety of coordination modes are adopted by NCS$:^-$: total coordination numbers vary from two to eight, with S and N coordination numbers going from zero to four (Fig. 2). In general, the sulfur terminus tends to adopt higher coordination numbers than the nitrogen terminus in the same compound. The differences in local bonding discussed also have consequences for their electronic structures and semiconducting properties.\textsuperscript{115}

1.2 Function

Metal thiocyanates have diverse functions. The most striking is undoubtedly the strong optical absorption and intense colours which arise largely due to the presence of low-lying metal-to-ligand charge transfer bands, e.g. the well-known blood-red ferric thiocyanate aqueous complex.\textsuperscript{22,23} The strong optical absorption has been harnessed for non-linear optical function,\textsuperscript{24} and photoconductivity.\textsuperscript{25} The magnetic properties of metal thiocyanates were originally of interest as susceptibility standards, due to the relatively temperature independent magnetic moment of ternary compounds such as CoHg(NCS)\textsubscript{4}. This arises because the large distances between ions produces weak magnetic superexchange and well isolated ions.\textsuperscript{26} However, long-range magnetic order has been found over comparable distances in Cr(Bi(SCN))\textsubscript{4} and even CoHg(NCS)\textsubscript{4} has surprisingly complex magnetism.\textsuperscript{26} Recent work has shown that metal thiocyanates possess a range of interesting magnetic behaviours, including magnetic order at liquid
nitrogen temperatures\cite{29} and low dimensional magnetism\cite{29,30}.
The presence of electronic communication between metal ions, despite the increased length of NCS$^{-}$, has also been harnessed to produce transparent conductors, e.g. Cu(NCS)\cite{31,32}. Thiocyanate compounds are also now being explored as catalysts for a range of reactions, including organophosphate hydrolysis and water photo-oxidation.\cite{33} The range of structures and chemistries suggests that future investigation of thiocyanates may uncover other novel functions.

2 Binary compounds

There are currently 23 binary metal thiocyanates with reported crystal structures (Fig. 1). They can be divided into five categories: van der Waals layered structures with octahedral metals analogous to the NiI$_2$ structure-type in halide (Section 2.1); 3D framework structures with eight-coordinate metals with highly distorted CaF$_2$-derived structures (Section 2.2); tetrahedral frameworks found for coinage metal monovalent cations related to CuI (Section 2.3); ionic structures analogous to NaCl and CsCl found for alkali metals and Ti$^+$ (Section 2.4) and a variety of complex, 1D, 2D and 3D frameworks adopted by groups 12, 14, and 15 metals (Section 2.5).

2.1 Ni(NCS)$_2$

The most common structure type for binary metal thiocyanates is the layered Ni(NCS)$_2$ structure, which is found for Ni, Co, Fe, Mn, Hg and Cu (Fig. 3). This structure is analogous to the CdI$_2$ structure type common for metal halides\cite{34} comprising layers of edge-sharing MN$_2$S$_4$ octahedra. The neutral layers are held together by van der Waals forces. The aristotype structure crystallizes in space group C2/m, lowered from the trigonal symmetry of the analogous halides due to the rod-like shape of thiocyanate. The M-SCN angle is around 100$^\circ$, and the M-NCS angle is roughly 160$^\circ$. Hg(II) and Cu(II) have structural deviations. For Hg(II), the tendency to lower coordination numbers and its soft nature means that there are two shorter Hg-S bonds, and four long Hg-N bonds, meaning there is instead HgS$_2$N$_4$ pseudo-octahedral coordination, or nearly linear HgS$_2$ coordination. Cu(II) thiocyanate has a pronounced Jahn-Teller distortion which lengthens one set of Cu-S bonds, lowering the symmetry to PT and producing a near one-dimensional structure. These compounds can in general be prepared by salt metathesis, either in water from metal sulfate and Ba(NCS)$_2$, or in an organic solvent from e.g. M(BF$_4$)$_2$ and KNCS, with the insoluble by-product filtered off and then the removal of the solvent from the filtrate containing M(NCS)$_2$. Typically this also requires desolvation of a solid solvate. Hg(NCS)$_2$ and Cu(NCS)$_2$ are both insoluble in water and can be prepared by direct reaction of a soluble metal salt and thiocyanate source. The synthesis of Cu(NCS)$_2$ can be challenging, due to the instability of this compound to Cu(NCS), and it can only be prepared at high concentrations. It will disproportionate on prolonged exposure to water forming Cu(NCS) and a mixture of by-products. The difficulty of preparing pure phase Cu(NCS)$_2$ meant its structure was determined 180 years after the first report of its existence.\cite{35,36}

Fe(NCS)$_2$ is the least chemically stable of the reported Ni(NCS)$_2$ structured frameworks, oxidising in air, although other compounds are sensitive to moisture: Mn(NCS)$_2$ is deliquescent and Co(NCS)$_2$ can be hydrated under humid conditions.\cite{29} Thermogravimetric analysis suggests these compounds are thermally stable in inert atmosphere up to approximately 300$^\circ$C,\cite{37} though Hg(NCS)$_2$ has long been known for its notable for its spectacular thermal decomposition in air to carbonitriles and mercury sulfides and oxides, the so-called ‘Pharaoh’s Serpent’ reaction.\cite{38,39}
These frameworks are also the only characterized binary thiocyanates containing paramagnetic ions (there are no magnetic measurements of Eu(NCS)$_2$). The first property measurements of Mn(NCS)$_2$, Ni(NCS)$_2$ and Co(NCS)$_2$ included magnetic susceptibility measurements over limited temperature range, which indicated significant antiferromagnetic interactions. Subsequent neutron diffraction revealed unusual layered antiferromagnetism in Ni(NCS)$_2$, and density functional theory calculations suggest these materials, like the analogous metal halides, may be delaminated to produce 2D magnets. Despite the propensity for transition metals to adopt a variety of oxidation states, only Cu has fully characterized compounds in an oxidation state other than +2 (Section 3.2). Hg(NCS)$_2$ has been reported to form, though nothing beyond their apparent composition is known. This family has series of unusual pharmacological functions, acting as both poacher and gamekeeper: Co(NCS)$_2$ can be used as a test for the presence of cocaine, and Cu(NCS)$_2$ in a component in salts designed to obscure the presence of the drug.

2.2 Ba(NCS)$_2$

The second most common structure type is the 3D Ba(NCS)$_2$ structure which forms for the alkaline earths Ca, Sr, Ba, and other large divalent cations such as Pb and Eu (Fig. 4). They all crystallize with the $C2/c$ space group and contain one crystallographically independent $M^{2+}$ cation and NCS$^-$ anion. Each M cation is coordinated by four N atoms and four S atoms in a distorted square antiprism. These polyhedra edge-share along the c-axis through N atoms, and corner-share in the ab-plane. Each NCS$^-$ anion is coordinated by four $M^{2+}$ cations in a distorted tetrahedron, and simplification of the structure by considering only the centre-of-mass of the NCS$^-$ anion reveals a distorted fluorite structure. These compounds can be synthesized by reaction between NaNCS and MCl$_2$ in sealed glass ampoules. Ba(NCS)$_2$, Ca(NCS)$_2$ and Pb(NCS)$_2$ can be formed through dehydration of the readily synthesizable hydrates. Ba(NCS)$_2$·3H$_2$O is a convenient starting point from any thiocyanate that is synthesized in water due to the insolubility of BaSO$_4$. Eu(NCS)$_2$ is the only known binary thiocyanate containing a paramagnetic ion that does not adopt the Hg(NCS)$_2$ structure, though its magnetic properties have not been reported. As an isotypic family, Eu(II) can be doped into the other non-fluorescent members hosts to produce materials with green fluorescence at low temperatures.

2.3 Coinage metals

The most polymorphic metal thiocyanates are the monovalent group 10 metals, Cu(NCS)$_2$ and Ag(NCS)$_2$, which have three and two distinct polymorphs (Fig. 5). Cu(NCS)$_2$ has tetrahedral Cu(I), coordinated by the S and one N atom, and equally each S atom coordinates to three Cu and each N to one Cu, i.e. NCS$^-$ is also tetrahedrally coordinated. Like other binary tetrahedral compounds this leads to extensive polymorphism. There are three reported crystal structures: orthorhombic $Pbca$ $\alpha$-Cu(NCS)$_2$, $P6_{3}mc$ $2\overline{H}$-$\beta$-Cu(NCS)$_2$ and $R3m$ $3R$-$\beta$-Cu(NCS)$_2$. All of these compounds have in common honeycomb-like CuS layers. $2\overline{H}$-$\beta$ and $3R$-$\beta$ have thiocyanates all point in the same direction, yielding polar structures, and in the $\alpha$ phase the thiocyanates alternate up and down in a stripe order pattern, producing a non-polar structure. The two distinct $\beta$ polymorphs (which have been confusingly allocated the same Greek letter label) differ only in the stacking of the CuS layers relative to each other, i.e. they are polytypes. $2\overline{H}$- $\beta$ has AB stacking, analogous to wurzite, and $3R$-$\beta$ has ABC stacking, analogous to spahelerite. The various polytypes are all slightly soluble in water, and can be prepared through various routes, including slow
evaporation of solutions of Cu(NCS) in aqueous Na(NCS) solution and spontaneous reduction of aqueous Cu(NCS)$_2$(NH$_3$)$_2$ solutions.  

There are no reports of phase transitions on heating or cooling in Cu(NCS), with powder diffraction measurements from 80 to 400 K on 2H-β showing no phase-change and modest thermal expansion, ($\alpha_\text{t} = 10.5 \text{MK}^{-1}$, $\alpha_\text{c} = -1.2 \text{MK}^{-1}$). Indeed, the thermal expansion is considerably smaller than predicted through DFT using the quasiharmonic approximation. High pressure Raman spectroscopy and powder X-ray diffraction measurements suggest that 2H-β phase transforms slowly into α above 4 GPa, before irreversibly amorphising through polymerization. Cu(NCS) is of particular interest as the extended CuS layers allow for significant electronic delocalization and hence p-type transparent conduction. Cu(NCS) is solution processable and has been explored as a hole transport layer in solar cells.

Ag(NCS) has two reported polymorphs. β-Ag(NCS) has a structured related to that of α-Cu(NCS) and comprises AgS$_3$N$_1$ tetrahedra connected by thiocyanate into a tetrahedral network, with a honeycomb type AgS layer with alternating up-and-down thiocyanates. α-Ag(NCS) contains AgS$_3$N tetrahedra, but is quite distinct from the other structures. The tetrahedra edge-share, and the bond lengths vary significantly. It can alternatively be thought of as consisting of 1D chains running along approximately the [010] direction, analogous to the structure of Ag(CN), connected by longer Ag-S into a 3D network. α-Ag(NCS) has a shortest Ag-Ag distance of 3.28 Å and two further Ag atoms at 3.30 and 3.41 Å, strongly suggestive of significant argentophilic interactions, common in the silver cyanides.

The argentophilic interactions form a 3D network with the srs or (10,a) topology and it is likely that these interactions are responsible for the unique structure of α-Ag(NCS). Ag(NCS) is very insoluble and can be prepared by precipitation from aqueous solution from soluble Ag$^+$ and NCS$^-$ salts. β-Ag(NCS) is favoured by rapid precipitation, acidification and the presence of gelatine. Variable temperature powder neutron diffraction study of the α phase on cooling shows small positive thermal expansion along the $a$ direction, and larger expansion along $b$ and $c$ directions (4.0 MK$^{-1}$, 30 MK$^{-1}$ and 54 MK$^{-1}$ respectively), but no phase transitions were observed down to 25 K.

### 2.4 Alkali metals

The structures and bonding of alkali metal thiocyanates are much more ionic than other metal thiocyanates (thallium has been included in this section due to the similarity of its chemistry) (Fig. 5). As metal pseudohalides, they adopt structures similar to the NaCl (Na, Li) and CsCl structures (K, Rb, Ti, Cs). The ionic bonding means that order-disorder transitions are a common feature of these compounds, like other metal pseudohalides, with phase transitions to plastic phases reported for K(NCS), Rb(NCS), Ti(NCS) and Cs(NCS). Phase transitions are reported to be absent for Na(NCS) on heating or cooling, or on pressure up to 4 GPa. Lithium thiocyanate is an Li ion conductor due to the presence of Li vacancies in typically synthesized samples. K(NCS), Rb(NCS) and Ti(NCS) all adopt the same ordered orthorhombic $Pbcn$ structure at room temperature, with eight coordinate NCS anions. On heating, $T_c = 415$ K for K, 434 K for Rb and 383 K for Ti. A high temperature $I4/mcm$ tetragonal structure forms, closely related to the low temperature form, but with head-tail disorder.

Cs(NCS) has, like the other larger metal thiocyanates, a structure related to the CsCl structure, with eight coordinate Cs$^+$ and NCS$^-$. However, both the low temperature ordered phase and high temperature phase are different from the K(NCS) structure type, with a more distorted low temperature $Pmca$ phase and a high temperature maximally symmetric $Pm3m$ cubic phase, with complete orientational disorder of the NCS$^-$ anion. The order-disorder transition is first order and the high temperature cubic phase transforms into a cubic phase shortly before melting.
phase exists only in a narrow temperature window, between 470 K and its melting point of 479 K. The symmetry relationships between the Cs(NCS) and K(NCS) structure types, and their phase transitions have been determined by Shlyaykher et al.\textsuperscript{82}

Na(NCS)\textsubscript{2} and K(NCS)\textsubscript{2} are both readily commercially available. Rb(NCS)\textsubscript{2} and Cs(NCS)\textsubscript{2} can be prepared either by reaction of NH\textsubscript{4}(NCS) with M\textsubscript{2}(CO\textsubscript{3})\textsubscript{2} in water, or by salt metathesis between M\textsubscript{2}(SO\textsubscript{4})\textsubscript{2} and Ba(NCS)\textsubscript{2}, and filtering off the insoluble BaSO\textsubscript{4}.\textsuperscript{11,12,29} Li(NCS)\textsubscript{2}·H\textsubscript{2}O is also commercially available, and the anhydride can be prepared through careful dehydration.\textsuperscript{73}

Although this review focuses on the solid metal thiocyanates, it is worth noting that the low melting points of inorganic metal thiocyanates mean that they have significant liquid state chemistry as molten salts/ionic liquids.\textsuperscript{84,91,22} Recent reports also suggest that solid solutions of Cu(I) and Zn(II) thiocyanates may also melt, though inhomogeneously.\textsuperscript{71}

2.5 p-block and late transition metals

The remaining binary metal thiocyanates, Sn(NCS)\textsubscript{2}, Bi(NCS)\textsubscript{3},\textsuperscript{15} Sb(NCS)\textsubscript{3},\textsuperscript{95} Cd(NCS)\textsubscript{2}\textsuperscript{96,97} and Zn(NCS)\textsubscript{2},\textsuperscript{98} each adopt a unique structures (Fig. 7). Zn(NCS)\textsubscript{2} has a tetrahedrally coordinated Zn, with two distinct sites, one ZnN\textsubscript{4} and the other ZnS\textsubscript{4}, and four distinct NCS\textsuperscript{−} anions each of which bridges two Zn atoms.\textsuperscript{29} This leads to a P\textsuperscript{1} van der Waals layered structure, analogous to the SiO\textsubscript{2} bilayer.\textsuperscript{99} The first report of the structure of Zn(NCS)\textsubscript{2} refers to it as β-Zn(NCS)\textsubscript{2}, which implies the existence of α-Zn(NCS)\textsubscript{2}, perhaps of lower symmetry, and although the analogy to SiO\textsubscript{2} suggests polymorphism is feasible, I have found no further details of an alternate phase.

Cd(NCS)\textsubscript{2} crystallizes in P\textsubscript{2}\textsubscript{1}/\textit{c} and has only a single Cd\textsuperscript{2+} site, octahedrally coordinated by thiocyanate to produce a trans-Cd\textsubscript{2}N\textsubscript{2} coordination polyhedron.\textsuperscript{96,97} Every thiocyanate has the S-terminus doubly coordinated, and the N-terminus singly coordinated. Thus far the description of Cd(NCS)\textsubscript{2} is identical to that of Ni(NCS)\textsubscript{2}, however in Cd(NCS)\textsubscript{2} there are two distinct NCS\textsuperscript{−} ions, and the overall connectivity of the framework is 3D. The structure is thus analogous to the MnO\textsubscript{2} ramsdellite or Al(OH)O\textsubscript{2} diaspore structure-types.\textsuperscript{100,101}

Sn(NCS)\textsubscript{2} adopts a unique structure and crystallizes in P\textsuperscript{\overline{4}} with a prominent stereochemically active lone pair.\textsuperscript{94} There is a single Sn ion, which is three-coordinate, SnN\textsubscript{2}S\textsubscript{1}, with one N-bound terminal NCS\textsuperscript{−}, and two bridging NCS\textsuperscript{−} anions. This produces a 1D coordination polymer connected into 2D sheets via weak Sn···Sn interactions, which might be considered ‘tetrel-bonds’.\textsuperscript{102} The low symmetry of the structure means that the bond lengths vary widely and alternative descriptions are admitted. Sn(NCS)\textsubscript{2} appears to be a promising electron-transport layer for photovoltaic devices.\textsuperscript{103,104} Tin(II) thiocyanate crystallizes from aqueous solution of Sn(SO\textsubscript{4})\textsubscript{2} and Na(NCS), whereas Zn(NCS)\textsubscript{2} and Cd(NCS)\textsubscript{2} can be prepared by salt metathesis between the metal sulfate and Ba(NCS)\textsubscript{2} in water.

Bi(NCS)\textsubscript{3} can be synthesized as an orange-yellow crystals through the slow evaporation of aqueous H\textsubscript{3}[Bi(SCN)\textsubscript{3}]\textsubscript{3} solutions obtained by the acid-base reaction between ethereal HSCN and Bi\textsubscript{2}O\textsubscript{3}(CO\textsubscript{3})\textsubscript{15}. Like Sn(NCS)\textsubscript{2}, it also has stereochemically active metal ions, crystallising in P\textsuperscript{\overline{1}}, however it is the most structurally complex of all the reported metal thiocyanate binaries, with two distinct metal ions and six distinct NCS\textsuperscript{−} ions.\textsuperscript{16} Both bismuth sites are very distorted, Bi\textsubscript{1} has four short bonds, Bi\textsubscript{2}N\textsubscript{3}S\textsubscript{2}, but including longer bonds can be considered to be seven coordinate, Bi\textsubscript{4}N\textsubscript{3}S\textsubscript{2}; Bi\textsubscript{2} considering short bonds is a very distorted octahedron, Bi\textsubscript{2}N\textsubscript{2}S\textsubscript{2}, but has an additional short contact to third N atom to make a seven coordinate (Bi\textsubscript{4}S\textsubscript{3}N\textsubscript{4}) coordination. These larger (seven vertex) polyhedra directly edge-share through one nitrogen and one sulfur, and are connected into a 3D framework through the length of the thiocyanates.

Sb(NCS)\textsubscript{3} can be obtained as colourless crystals by removing THF from the relevant solvate, itself synthesized from the reaction of SbF\textsubscript{3} and trimethylsilyl isothiocyanate.\textsuperscript{95} It crystallizes in the high-symmetry yet polar I\textsubscript{4}1cd space group, with a very significant stereochemically active lone pair. Considering only the shortest bonds it can be thought of as comprising solely of molecular Sb(NCS)\textsubscript{3} units. If slightly longer (3.1 Å) Sb-S bonds are considered, the Sb(III) cation has distorted octahedral coordination, Sb\textsubscript{3}N\textsubscript{3}S\textsubscript{3}. These octahedra edge-share (through the length of the thiocyanate) to form infinite chains. These chains corner-share (though only on alternate layers) to form a 3D network. For these main-group and d\textsuperscript{10} transition metal elements, the lack of crystal-field stabilization energy appears to permit a much wider variety of structure types, and indeed the presence of significant stereochemically active lone pairs in Sn(II), Sb(III) and Bi(III) produces the most complex reported binary metal thiocyanate structures.

2.6 Missing binary thiocyanates

The above compounds are the 23 binary metal thiocyanates with reported crystal structures. Nearly all stable (and some radioactive) metals have been reported to form complexes with thiocyanate,\textsuperscript{81} and it is likely stable binary metal thiocyanates can also be formed for nearly all metals too. Indeed, 13 further metallic elements have been reported to form binary thiocyanates, leaving only 24 non-radioactive metallic elements with no reports at all (Fig. 1). The 37 binary metal thiocyanates without structures are likely challenging to synthesize in part due to the need to simultaneously bond both ends of the thiocyanate with their different chemistries, and the propensity to form stable solvates rather than extended frameworks. Below I briefly outline the missing 37 binary metal thiocyanates, and where their synthesis and compositions has been reported, the current state of knowledge. The lack of full characterization for many of these compounds means that these should be treated with caution. Even in materials without complete characterization it is notable that there are currently very few reports of variable oxidation states in metal thiocyanates, even though it is likely that multiple oxidation states of some binaries can be prepared (particularly of transition metal thiocyanates).

The first class of missing binaries are those formed from the hard, oxophilic metals, where although M-NCS bonds are facile to form, M-SCN is not competitive with most solvents. There are two missing group 2 thiocyanates, Be(NCS)\textsubscript{2} and Mg(NCS)\textsubscript{2}. Beryllium thiocyanate complexes are known,\textsuperscript{105} but the solid state
preparation has rarely been attempted, and appears to be chal-
gen[8]ing. Mg(NCS)2 · xH2O has been extensively studied and investigation of its dehydration suggests that preparation of the anhydrate from the hydrate is not feasible and previous reports of Mg(NCS)2 were erroneous. Likewise the oxophlicity of group 3 and lanthanide elements means hydrates are readily formed. Attempts to synthesize Sc(NCS)3 from solution readily produce solvates of stoichiometry Sc(NCS)3L2, though a poorly characterized ‘yellow scandium trithiocyanate’ has been hinted at. Other group 3 and lanthanide binary thiocyanates are unknown, though many octahedral molecular solvates Ln(NCS)3L2 and homoleptic anionic complexes with N-bound thiocyanate have been reported.

Moving right along the periodic table, the synthesis of Ti(NCS)4 has been reported by the desolvation of THF solvates at 150°C under vacuum, producing a red-black crystalline powder. Analysis of the IR spectrum of Ti(NCS)4 suggests octahedrally coordinated Ti cations with at least some bridging NCS− anions. These data thus imply the structure is more similar to TiF6 4−, a 1D structure comprising corner-sharing TiF6 octahedra, rather than the later halides, TiX4, X = Cl, Br, I, which are all tetrahedral molecular materials, with no Ti–X–Ti bridges. There are no reports of Zr(NCS)4 or Hf(NCS)4, though the DMF solvates of both are reported. It is worth noting that one of the few ways to readily separate Zr and Hf is by preparing the thiocyanato oxo-hydroxy metal complexes, and so it is possible that Zr(NCS)4 and Hf(NCS)4 will have different structures and chemistries.

All binary group 5 thiocyanates are attested, with the most thoroughly investigated being V(NCS)3, which can be made through salt metathesis in diethyl ether between NaNCS and VCl3, producing a red-brown powder. V(II) and V(IV) thiocyanate complexes are also stable, though only solvates have been reported. Nb(NCS)3 and Ta(NCS)3 are reported to be dimers on the basis of IR spectroscopy, and were prepared by desolvation of the acetonitrile solvates.

Group 6 binary thiocyanates are less well understood. Cr(NCS)3L2 is well known for a range of solvents, but the anhydride has not proved possible to prepare, likely in part due to the high sensitivity of Cr(II) to oxidation. Cr(NCS)3 is reported to be a deliquescent dark green powder, though characterization is scant. A variety of solvated Mo(V) and W(VI) thiocyanates can be made through the reaction of K(NCS) or Na(NCS) with MoCl5 and WCl6 in organic solvents forming dark red (Mo) or dark brown (W) crystals, but desolvation was not possible by applying a vacuum. Oxothiocyanato metal complexes are common in these high oxidation states, but lower oxidation-state molecular molybdenum and tungsten thiocyanate complexes with coligands and/or additional counter cations are common and can include metal-metal bonding. DFT investigations of the binary Mo(NCS)2 and W(NCS)2 suggest they are stable and adopt layered structures, analogous to the Hg(NCS)2 structure, though with trigonal prismatic metal coordination and metal-metal bonding. The computational stability of these hypothetical layered structures relative to cluster structures, e.g. a M6(NCS)12 hexametallic cluster, is not reported, despite these being the stable structures of the analogous halides.

The 3d late transition metals all form divalent binary thiocyanates with the Ni(NCS)2 structure, as described above, though other oxidation states are unknown except for hints of Fe(NCS)3. The late 4d- and 5d-block binary metal thiocyanates are much less well understood in contrast. Technetium and rhenium thiocyanate complexes are known in a variety of oxidation states, but there are no reports of the binary compounds aside brief discussion of an orange-red solid complex.
formed on reaction of ReO₄ with KNCS and SnCl₂, of probably composition Re(NCS)₄ or ReO(NCS)₄.[135,137]

Rh(NCS)₂ is reported to be a brown powder formed by the reaction of Rh₂(CCl₄COO)₂₄ dimers with potassium thiocyanate which is insoluble in water, though the presence of an infra-red absorption band at 1614 cm⁻¹ suggests perhaps more extensive reaction than simple salt metathesis has occurred.[138] The synthesis of Rh(NCS)₃ and Ru(NCS)₃ as orange-red (Rh) and dark brown (Ru) powders from the salt metathesis in acetonitrile between K(NCS) and the metal trihalide has been reported.[139,140] There are no reports of the synthesis of binary Os(NCS)x or Ir(NCS)x though both are likely to be stable in the +3 oxidation state as implied by the existence of molecular [M(NCS)₆]³⁻ anions.[141] I note that Os(NCS)₃ is likely to be the best candidate for a magnetic ReO₃-structured metal thiocyanate as it has the most extensive linkage isomerism with thiocyanate of any paramagnetic metal.[142]

Pd(NCS)₂, Pt(NCS)₂ and Au(NCS) have all been reported and chemical elemental analysis suggests they are pure phase compounds. Pd(NCS)₂ and Pt(NCS)₂ are reported from the thermal decomposition of M(NCS)₂(NH₃)₂.[143,144] Aurous thiocyanate has also been reported to form as a white powder by thermal decomposition of the organometallic complex [Et₂Au(NCS)₂] through addition to hot xylene (125°C). Warning: the decomposition of the solid [Et₂Au(NCS)]₂ at temperatures above 80°C is reported to be explosive.[145] Au(NCS)₃ has been reported to form from the reaction of excess AuCl₃ with soluble alkaline metal thiocyanate salts, though further detail of the synthesis and characterization is unreported.[146]

The only crystal structure of a group 13 binary thiocyanate is Ti(NCS)₃; however many more should exist. A number of routes for the synthesis of In(NCS)₃ have been reported: salt metathesis in ethanol between Na(NCS) and InCl₃; metathesis in water between Ba(NCS)₂ and In₂(SO₄)₃; reaction between In metal and Hg(NCS)₂; and sulfuration of In(NCN)₃.[147,148] Analysis of X-ray powder diffraction measurements suggests cubic cell of 12 Å, which implies a ReO₃-type model consisting of alternating In₈ and InS₆ octahedra, though there is no atomic structural model or quantitative refinement of the diffraction data.[149] This structure would be related to the observed CsCd(NCS)₃ structure (Section 3.1). An analogous route to create Ga(NCS)₃, that is the aqueous metathesis reaction between Ba(NCS)₂ and Ga₂(SO₄)₃, produced a hydrate with N-bound thiocyanate which could not be further dehydrated.[150] The formation of a stable N-bound thiocyanate hydrate is also reported for aluminium, though again dehydroxylation was not possible.[151] The potential for Ti(III) or In(I) thiocyanates has not been extensively explored, though the aqueous reaction of TiCl₃ with KNCS has been reported to oxidize NCS⁻ to HCN and H₂SO₄.[152]

In addition to the well-known Pb(NCS)₂ and Sn(NCS)₂, group 14 metal thiocyanates with +4 oxidation state should be feasible. Sn(NCS)₄ is reported to form from the reaction of thiocyanoen (NCS)₂ and Sn(OH)₄ in ethereal solution, though without any further characterization.

3 Ternary Metal Thiocyanates

In addition to the binary metal thiocyanates outlined above, there are many more solid-state inorganic metal thiocyanates with more complex compositions. In this review I have restricted discussion to the ternary homoleptic thiocyanates, AₓMₓ(NCS)₃, as they illustrate the distinctive features of metal thiocyanate chemistry. Ternary thiocyanates can be broadly classified by the dimensionality of the coordination framework: 3D-, 2D- and 1D-connected frameworks, and 0D salts containing only discrete metal thiocyanate complexes.

3.1 3D: Perovskitoid

There are two main families of 3D frameworks which can be realized for a wide range of compositions: perovskitoid, based on octahedrally-coordinated metals, and diamondoid, based on tetrahedral metals. In common with other metal thiocyanates, the different chemistries of the N and S termini is key, and means that in both cases, ‘double’ structures with alternating cation–order predominate. The distinctiveness of each end of the ligand means all reported metal thiocyanate perovskitoid and diamondoid structures are containing alternating Mn₆ and Ms₆ polyhedra. This means most of these materials use two different framework-forming metal ions: a harder metal for the Mn₆ polyhedron, and a softer metal for the Ms₆ polyhedron.

The perovskitoid structures comprise corner-sharing octahedra linked by a single μ₁₁ coordinated thiocyanate potentially with cations contained with the pseudocubic cavity (Fig. 7). Like the non-molecular perovskitoid analogues, these metal thiocyanates are extremely diverse family. I have also included here some perovskitoids of more complex stoichiometry, to situate the chemistry of these materials within the broader family and highlight some of the unique structural features. The limited range of softer metals means currently known NCS-perovskitoids can be classified into three families by the identity of the Mn₆ cation: AₓMₓ[Pt(SCN)₆]₃, AₓMₓ[Pt(SCN)₆]₃ and AₓMₓ[CD(SCN)₆]. The occupancy of A site cation varies from x = 0, (i.e. an ReO₃ or Prussian Blue type structure), to x = 2, the standard perovskite stoichiometry.

The very first known perovskitoids were M[Pt(SCN)₆], M = Fe, Cu, Co, reported by Buckton in 1856.[153] Though the stated stoichiometry was wrong due to the incorrectly determined masses of N and S at the time, and the lack of structural characterization techniques available at the time precluded an understanding of its perovskitoid structure. Recent work has determined the structures of not only these, but also M = Mn and Ni.[154] Although Buckton’s initial report was understandably lacking in diffraction-based characterization, it did include an unlikely to be replicated thorough gustatory characterization, highlighting the “exceedingly nauseous taste” of soluble [Pt(SCN)₆]⁴⁻ compounds. In addition to the perovskitoid structured compounds, Buckton also reported K₂[Pt(SCN)₆] (Buckton’s salt), now partially structurally determined (Section 3.6). and otherwise unknown compounds of [Pt(SCN)₆]⁴⁻ with Hg, Ag, Pb and Au. Other platinum-based perovskitoids are very likely feasible.[155]

The first metal thiocyanate perovskitoid to have its structure
Fig. 8 Structures of perovskite thiocyanates $A_2[M^+\{SCN\}_6]$ form, all with rock-salt M site order. (a) The three classes of perovskite, with $M=\text{Pt}^{4+}$, $\text{Bi}^{3+}$ and $\text{Cd}^{2+}$. (b) Complex A-site cation order in $(\text{CH}_3\text{NH}_3)_2[Ni\{\text{Bi} \{\text{SCN}\}_6\}]^{153}$ (c) Ordered $[\text{Bi} \{\text{SCN}\}_6]^{3–}$ in $(\text{NH}_4)_4\{\text{Ni}\{\text{Bi} \{\text{SCN}\}_6\} \cdot \frac{5}{6} \text{H}_2\text{O}}^{153}$ (d) A-site cation orientational order transition in $(\text{NH}_4)_2\{\text{Ni}\{\text{Cd} \{\text{SCN}\}_6\}]$ by tilt.

determined was $\text{CsCd}(\text{NCS})_3$ and it is unusual. Rather than having distinct hard and soft cations on the $\text{M}_6$ and $\text{MS}_6$ sites, it has Cd ions on both. The Cs$^+$ cation reside in the pores of the anion framework.$^{159}$ Larger cations can also be incorporated within this framework, as shown by $[(\text{CH}_3)_2\text{S}]_2\{\text{Cd} \{\text{SCN}\}_6\}]_6^{157}$ Cadmium thiocyanate perovskitoids can also occur with mixed metals, where the $\text{M}_6$ site is occupied by a harder first-row transition metal, including $A_2\{\text{Ni} \{\text{Bi} \{\text{SCN}\}_6\}] \ A = \text{K}, \text{NH}_4, (\text{CH}_3)_2\text{NH}_2$ and $[(\text{CH}_3)_2\text{NH}_2]_2\{\text{Mn} \{\text{SCN}\}_6\}]_6$.\(^{156,157}\)

The use of $\text{Cr} \{\text{Bi} \{\text{SCN}\}_6\}]_6$ to quantitatively analyse the presence of bismuth in solution date from the 1930s\(^{161}\) but its structure was determined only recently, together with the isostructural $\text{Sc} \{\text{Bi} \{\text{SCN}\}_6\}]_6$ and $\text{Fe} \{\text{Bi} \{\text{SCN}\}_6\}]_6$.\(^{15}$ Other bismuth-based perovskitoids containing divalent transition metals and A-site cations are now known, including both $A\{\text{Ni} \{\text{Bi} \{\text{SCN}\}_6\}]_6$, $A = \text{K}, \text{NH}_4$ and $\text{CH}_3\text{NH}_2$, and more complex stoichiometries: $\text{C}(\text{NH}_3)_2\{\text{Ni} \{\text{Bi} \{\text{SCN}\}_6\}]_{3/6}$, $\text{Mn}_2\text{Bi}_2(\text{NCS})_7 \cdot 7\text{H}_2\text{O}$, $\text{Co}_2\text{Bi}_5(\text{NCS})_{36} \cdot 38\text{H}_2\text{O}$, $\text{M}_6\text{Bi}_5(\text{NCS})_{30} \cdot 16\text{H}_2\text{O}$, $3\text{NH}_4 \text{M} = \text{Ni}$, Co.\(^{154,155}\)

As perovskitoids, multiple orderings lowering the symmetry from the $Pnma$ naturally arise. Rocksalt ‘M’ site order is strongly enforced in all known NCS perovskitoids, due to the preference for $\text{M}_6$ and $\text{MN}_6$ octahedra. The fact that the S-terminus binds in a bent fashion imposes large cooperative tilts, meaning that NCS perovskitoids have tilts along every axis, which combined with the presence of the rocksalt order means only six simple tilt-sequences are possible, in the Glazer notation $a^+a^-a^+$, $a^+a^-b^+c^+$, $a^-a^-a^– $, $a^-b^-b^–c^–$, $a^+b^-b^-a^+c^+$, $a^+b^-c^+a^– $.\(^{162,163}\) Of these, the $\text{M}[\text{Pt} \{\text{SCN}\}_6]$ perovskitoids adopt the $a^+b^-c^–$ sequence and most $\text{M} \{\text{Bi} \{\text{SCN}\}_6\}]_6$ and $\text{M} \{\text{Cd} \{\text{SCN}\}_6\}]_6$ compounds adopt the $a^–b^–c^+$ sequence.\(^{16}$ As the sulfur bond angle guarantees a tilted structure, larger cations (e.g. molecular cations) induce complex tilts, e.g. $\text{CH}_3\text{NH}_3\{\text{Ni} \{\text{Bi} \{\text{SCN}\}_6\}]_6$ adopts the $a^–b^–c^+$ tilt, or cation vacancies, e.g. $\text{C}(\text{NH}_3)_3\{\text{Bi} \{\text{SCN}\}_6\}]_{15/6}$ to accommodate them.\(^{154}\) The greater coordinative flexibility of perovskites with $\text{Cd} \{\text{NCS}\}_6$ or $\text{Mn} \{\text{NCS}\}_6$ octahedra, allows for unconventional tilts and columnar shifts (a degree of freedom impossible in non-molecular perovskites),\(^{154,156}$ particular in the presence of larger cations, whether molecular or Cs$^+$\(^{153,157}$ $(\text{CH}_3)_2\text{S})^+$ is the largest ‘A’ site cation reported in a thiocyanate perovskitoid, and when even larger cations are used which cannot be included within the cages non-perovskite phases start to form, most typically a 1D face-sharing chain $\text{CaNiCl}_2$-analogue structure type.\(^{167,169}\)

There are also potential orderings associated with the A-site. In general, molecular A-site cations are orientationally ordered due to the low-symmetry of the frameworks,\(^{154}$ but an order-disorder phase transition has been found in $(\text{NH}_4)_2\{\text{Ni} \{\text{Cd} \{\text{SCN}\}_6\}]_6$,\(^{158}$ and A-sites are often disorderd in frameworks containing B-site vacancies.\(^{154,155}$ In perovskites with partial occupancy of the A-site, the tilts strongly couple to the A-site order, producing complex orders not found in non-molecular perovskites, which have the potential to produce electrical polarity.\(^{154}\)

3.2 3D: Diamondoid

For tetrahedral metals bound by thiocyanate, the 1:1 hard:soft stoichiometry typically produces a diamond net, comprising alternating MN$_4$ and MS$_4$ tetrahedra (Fig. 9). This structure type...
was first determined by Jeffery for CoHg(SCN)$_4$, historically widely used in microanalysis and as a calibrant for measures of magnetic susceptibility, though there is both a significant easy-plane zero field splitting, with $D = +10.6(5)$ cm$^{-1}$, and weak superexchange $\mathcal{J} = -0.2(1)$ cm$^{-1}$. As this family crystallizes in the polar $I$ space group, these compounds are also of interest for their non-linear optical properties, particularly ZnHg(SCN)$_4$.

The crystal structure of a related composition, NiHg(SCN)$_4$ in each structure. The topologies by NCS AgS the NCS ligands, but each S atom is shared between two Cu(NCS).

There are a number of other more complex, 3D framework structures reported, formed from a mixture of tetrahedral and octahedral cations or other coordination geometries, though connections to the perovskitoid and diamondoid can often be made (Fig. 10). ZnAg(SCN)$_4$ is polymorphic, with both polymorphs assembled from ZnN$_6$ tetrahedra and BiS$_6$ octahedra connected by NCS$^-$, with multiple symmetry independent Bi and Zn sites in each structure. The topologies (clw1 and clw2) of these two structures are otherwise unknown in the ToposPro database. $\alpha$-Zn$_3$Bi$_2$NCS$_6$ is of particular interest as it can be thought of as comprising Zn[Bi(SCN)$_4$]-perovskite layer, with every other layer containing an addition Zn$^{2+}$ cation connecting them.

Zn[Ag$_2$(SCN)$_4$] is assembled from corner-sharing ZnN$_4$ and AgS$_4$ tetrahedra which are connected through the length of the NCS ligands, but each S atom is shared between two AgS$_4$ tetrahedra, meaning NCS$^-$ is three coordinate. The extended inorganic connectivity is reminiscent of semiconducting Cu(NCS)$_2$.

### 3.3 3D: Other Structures

There are a number of other more complex, 3D framework structures reported, formed from a mixture of tetrahedral and octahedral cations or other coordination geometries, though connections to the perovskitoid and diamondoid can be often be made (Fig. 11). Zn[Co(SCN)$_4$], is polymorphic, with both polymorphs assembled from ZnN$_4$ tetrahedra and BiS$_6$ octahedra connected by NCS$^-$, with multiple symmetry independent Bi and Zn sites in each structure. The topologies (clw1 and clw2) of these two structures are otherwise unknown in the ToposPro database.

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### 3.4 2D Layers

There are a number of different ternary metal thiocyanates with primarily 2D connectivity (Fig. 11). The most widely explored is the post-perovskite structure, first reported for Rb[Co(SCN)$_4$], and later expanded to Cs[M(NCS)$_3$], where M = Ni, Co.
These materials, like the perovskites, are formed from two different metal coordination environments, but in this case they are MS\textsubscript{3}N\textsubscript{4} and MS\textsubscript{3}N\textsubscript{2}. These polyhedra edge-share through the length of the NCS\textsuperscript{−} ligand with polyhedra of the same kind and corner-share with the others, to form anionic sheets of composition [M(NCS)\textsubscript{3}]\textsuperscript{−}, with the counter-cation lying between them. The post-perovskite oxides and halides are typically formed at GPa to 100 GPa pressures, e.g. MgSiO\textsubscript{3}\textsuperscript{[193,194]} CaIrO\textsubscript{3}\textsuperscript{[195]} and NaMn\textsubscript{3} (M = Mg, Zn, Ni, Co, Fe)\textsuperscript{[196,200]} and so the relative accessibility of thiocyanate post-perovskites has allowed for more detailed investigation of their magnetism\textsuperscript{[81]}. 

Pb[Zn(NCS)\textsubscript{4}]\textsubscript{2} comprises Pb(SCN)\textsubscript{6} octahedra and Zn(NCS)\textsubscript{4} tetrahedra, both significantly distorted and connected into neutral layers\textsuperscript{[83]}. Unlike the other discussed ternaries thus far, there are direct Pb–S–Pb connections in this structure and the PbS\textsubscript{2} substructure thus resembles a 2D perovskite with (110) type layers, e.g. the MnF\textsubscript{2} substructure in BaMnF\textsubscript{4}\textsuperscript{[201]}.

MnHg\textsubscript{2}(SCN)\textsubscript{6} has a large number of distinct metal environments, with four different Hg sites and two different Mn sites\textsuperscript{[150]}, All Hg atoms form part of Hg\textsubscript{2}(SCN)\textsubscript{6} dimers of tetrahedra, with one dimer consisting of edge-sharing Hg(SCN)\textsubscript{4} tetrahedra linked through the S atoms, and the other containing one Hg(SCN)\textsubscript{4} tetrahedron and one Hg(NCS)\textsubscript{3} tetrahedron, edge-sharing with one M-S-M bridge and one M-SCN-M bridge. One Mn is octahedrally coordinated and the other has unusual square pyramidal coordination. The Hg\textsubscript{2} dimers when considered as a unit are five or six coordinate, like the Mn ions, and are connected in an alternating fashion through the length of the thiocyanate ligand. The Hg\textsubscript{2} and Mn coordination polyhedra edge-share along the c-axis, but are corner-sharing along the a-axis. The five coordinate square pyramidal Mn and the five-coordinated Hg\textsubscript{2} dimer are aligned along the a-axis and hence only have half the interchain connections due to their reduced coordination numbers. The layer structure can therefore be related to the M(NCS)\textsubscript{3} layer found post-perovskite structure, though with considerable additional structural complexity.

K[Ag(SCN)\textsubscript{3}] is formed from AgS\textsubscript{4} tetrahedra which edge-share through the S atom to create dimers, and then these dimers corner-share through the S atom to form infinite anionic sheets. The N-termini of the NCS\textsuperscript{−} anions point into the interlayer gallery towards the K atoms\textsuperscript{[202,203]}.

### 3.5 1D Chains

Low-coordinate soft metals can, in the right stoichiometry, form 1D structures with thiocyanate and alkali metals (Fig. 12). Rb\textsubscript{2}[Ag(SCN)\textsubscript{3}] comprises a 1D chain of corner-sharing AgS\textsubscript{4} tetrahedra\textsuperscript{[204]}. Similarly, Rb[Hg(SCN)\textsubscript{3}] consists of chain of corner sharing Hg\textsubscript{2} tetrahedra connected through the S-atom of the NCS\textsuperscript{−} ligand\textsuperscript{[153]}, Cs[Hg(SCN)\textsubscript{3}] also has a chain structure of tetrahedra, but in this case, the tetrahedra edge-share through S to form Hg\textsubscript{2}S\textsubscript{2}N\textsubscript{2} dimers, which are connected through the length of thiocyanate to form extended 1D connectivity\textsuperscript{[153]}.

The isostructural family M[Au(SCN)\textsubscript{3}]\textsubscript{2} M = K, Rb, Cs, have an very different kind of chain structure, comprising linearly coordinated Au(I) anions [Au(SCN)\textsubscript{3}]\textsuperscript{−} stacked and connected by aurophilic interactions, with a slight alternation of Au-Au distance e.g. for K[Au(SCN)\textsubscript{3}]\textsubscript{2} \(d_{\text{Au-Au}} = 3.04 \pm 3.00 \text{ Å}\)\textsuperscript{[205]}, Different M cations lead to slightly different \(d_{\text{Au-Au}}\), which in turn produces differences in the optical fluorescence.

### 3.6 0D Salts

The final class of ternaries are those with no extended coordination, which can be called salts, or vacancy-ordered derivatives of framework-structures as appropriate (Fig. 13). Coordination to alkali metals is neglected as the bonding is primarily ionic, non-directional and hence not framework-forming. Anionic homolectic metal thiocyanate complexes are probably the most diverse family of metal thiocyanate compounds, but reported crystal structures typically include organic counterions or solvent\textsuperscript{[206,207]}. There are thus surprisingly few crystal structures of purely inorganic ternary thiocyanate salts.

Most 0D metal thiocyanate structures have isolated metal centres, but there are two reported structures containing dimerized Ag(I) tetrahedra, Cs\textsubscript{2}[Ag(SCN)\textsubscript{3}] and K\textsubscript{2}[Ag(SCN)\textsubscript{3}], comprising edge-sharing AgS\textsubscript{4} tetrahedra, stabilized by intradimer argentophilic interactions\textsuperscript{[202,204]}. The most diverse class of salts contain octahedrally coordinated metals, i.e. [M(NCS)\textsubscript{3}](SCN)\textsubscript{6-x}\textsuperscript{−} anions, for which crystal structures exist for \(x\) from 2 to 4, and for \(x = 0\) or 6, other values are reported with organic cations and solvates. Na\textsubscript{6}[Mg(NCS)\textsubscript{6}] has a trigonal structure, \(\text{P}3\text{I}1\text{c}\), built from two kinds of layers, the first composed of alternating [Mg(NCS)\textsubscript{6}]\textsuperscript{4−} and Na\textsuperscript{+} cations and the second containing just Na\textsuperscript{+} cations. CS\textsubscript{3}[Mo(NCS)\textsubscript{6}] is hexagonal, with columns of [Mo(NCS)\textsubscript{6}]\textsuperscript{3−} anions with Cs\textsuperscript{+} cations in between. The crystal structure shows very significant disorder which remains present down to 115 K\textsuperscript{[213]}, K\textsubscript{3}[Rh(SCN)\textsubscript{6}], despite the compositional similarity adopts a different structure.
The chemistry of known metal thiocyanates is very rich and despite this richness, there are likely many more compounds to be discovered. The binary compounds presently known can be separated into five broad categories: the layered octahedral structures derived from the Ni(NCS)$_2$ structure type; the distorted fluorite eight-coordinate structures analogous to Ba(NCS)$_2$; the polymorphic tetrahedral structures found for Cu(I) and Ag(I); the ionic NaCl and CsCl derived structures found for group 1 and Tl$^+$ thiocyanates; and the complex framework structures found for the d$^{10}$ and p-block metals. These categories will likely become clearer as more structures are discovered, and there are 37 metal thiocyanates yet to be structurally characterized, of which 24 have not yet been reported at all.

Ternary thiocyanates naturally adopt a wider range of structures than the binaries. Two general themes are the prevalence of perovskitoid and diamondoid structures and the frequency with which a mixture of soft and hard metals occurs. There are undoubtedly many more ternary structures feasible, let alone quaternary or higher order compositions. The complexity of some of these structures is such that crystallography has been essential with isolated [Rh(SCN)$_6$]$^{3-}$ anions, but the structure (due to limitations of contemporary crystallography) has no information about the SCN$^-$ ligand location.$^{214}$ The limitations of historic crystallographic analysis unfortunately also affect K$_2$[Pt(SCN)$_6$] and Rb$_2$[Pt(SCN)$_6$], which are isostructural and crystallise in the space group P$^3_m1$. The thiocyanate anions cannot be resolved, but the arrangement of the alkali cations and [Pt(SCN)$_6$]$^{3-}$ anion is likely an anti-CdI$_2$ structure type.$^{215}$

Next, there are four reported crystal structures with four coordinate metals, tetrahedral K$_2$[Hg(SCN)$_4$]$^{206}$ and K$_3$[Ag(SCN)$_4$]$^{202}$ and the square-planar isostructural K$_2$[Pd(SCN)$_4$]$^{209}$ and K$_2$[Pt(SCN)$_4$]$^{207}$, both of which have weak axial M-S bonds which would connect the square planar units into chains.

The final family of coordination complexes are the eight coordinate f-block metals. Cs$_3$[Nd(NCS)$_8$]$^{8+}$ has a NdN$_8$ coordination geometry intermediate between cubic and square antiprismatic,$^{213}$ whereas Cs$_4$[U(NCS)$_6$]$^{4+}$ has a square antiprismatic UN$_6$ coordination.$^{209}$ Both crystallize with isolated anions in tetragonal space groups, Nd in $I\bar 4$ and U in $P4/n$.

In addition to these simple salts, there are complex salts for which there are additional isolated thiocyanate ions, alongside the thiocyanatometallate complexes. Cs$_3$[Co(NCS)$_4$]$_4$(NCS) contains, in addition to the tetrahedral [Co(NCS)$_4$]$^{2-}$ anions which stack on top of either other, free NCS$^-$ anions,$^{211}$ K$_2$Li(NCS)$_3$ crystallizes in polar $Pna2_1$ space group, with the polarity largely arising from the arrangement of NCS$^-$ anions. If coordination bonds between the alkali metals and NCS$^-$ were considered, the structure could instead be thought of as a chain structure with LiN$_3$S tetrahedra bridged into chains through the length of a NCS$^-$ ligand. Each individual chain is polar and each chain has the same polarity.$^{219}$

4 Conclusion

The chemistry of known metal thiocyanates is very rich and despite this richness, there are likely many more compounds to be discovered. The binary compounds presently known can be separated into five broad categories: the layered octahedral structures derived from the Ni(NCS)$_2$ structure type; the distorted fluorite eight-coordinate structures analogous to Ba(NCS)$_2$; the polymorphic tetrahedral structures found for Cu(I) and Ag(I); the ionic NaCl and CsCl derived structures found for group 1 and Tl$^+$ thiocyanates; and the complex framework structures found for the d$^{10}$ and p-block metals. These categories will likely become clearer as more structures are discovered, and there are 37 metal thiocyanates yet to be structurally characterized, of which 24 have not yet been reported at all.
to determine the basic chemistries, with simple IR spectroscopic rules of thumb sometimes being misleading.

Making connections between molecular framework and atomic inorganic materials can be very productive, both better to understand the structures of molecular framework materials and also to suggest potential structure-types that have not yet been realized in functional materials. Notably, none of the missing binary thiocyanates are present in the extremely large hypothetical alized in functional materials. Notably, none of the missing bi-
ter monolayer materials (M(NCS)) and ternary thiocyanates which are structurally two-dimensional thermodynamically despite their synthetic accessibility. This review also highlights that the experimental literature continues to offer opportunities to discover new functions through reinvestigation of known materials. For example there are nine binary and ternary thiocyanates which are structurally two-dimensional with neutral layers but that have not been investigated as potential monolayer materials (M(NCS)) and more than half of these have not been previously proposed to be stable as monolayers theoretically. This suggests that the chemical insight and deep searching of chemical literature can still be a fruitful route for uncovering brand new materials and useful functionality. In particular, although the majority of materials described in this review were described using salt-metathesis, alternative synthetic routes, whether classical or using more modern techniques, could allow for the realization of presently unknown compounds.

This review builds on the book of Golub, Köhler and Skopenko, last updated in 1986, and our structural understanding of this family has dramatically improved over the intervening decades due to dedicated efforts of synthetic inorganic chemists and the significant advances in characterization. I anticipate that the continuing efforts of chemists, supported by the growing power of computation, means that a review of metal thiocyanates in 2060 will be much broader in the chemistry and deeper in its under-

Conflicts of interest
No conflicts of interest to declare.

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Author Contributions
Notes and references


