

Cite this: DOI: 00.0000/xxxxxxxxxx

Inorganic Metal Thiocyanates

Matthew J. Cliffe*¹Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

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,^{1,2} most commonly as a ligand in molecular metal complexes*,³ but also as an organic functional group⁴, in biological chemistry as a key metabolite⁵ with potential anticarcinogenic function⁶, and even in space⁷. 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.^{8,9} In this pioneering work, Porrett used HNCS to prepare 'sulferetted chyzate' 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.⁸ 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, Al 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)¹⁰ to highly radioactive compounds (*e.g.* EsCl₃).¹¹ 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.^{3,12,13} 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)¹⁴ and Williams (1948),¹⁵ 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-

¹ School of Chemistry, University Park, Nottingham, NG7 2RD, United Kingdom Email: matthew.cliffe@nottingham.ac.uk

* As is standard, where thiocyanate is bonded purely through N it has been written as M(NCS)_x, and when through S as M(SCN)_x. In most of the described binary frameworks thiocyanate is both N- and S-bound and for these M(NCS)_x is used without implying anything about the local bonding.

† Other older trivial names for thiocyanate include rhodanide and sulfocyanide.

Structure Determined			Composition Reported			Unknown			Nonmetal/ Radioactive									
hydrogen 1 H 1.0079												helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122									boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180			
sodium 11 Na 22.990	magnesium 12 Mg 24.305									aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948			
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.798	
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.96	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29	
caesium 55 Cs 132.91	barium 56 Ba 137.33	lanthanum 57 La 138.91	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]	
francium 87 Fr [223]	radium 88 Ra [226]	actinium 89 Ac [227]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [277]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [271]	roentgenium 111 Rg [272]	copernicium 112 Cn [285]	nihonium 113 Nh [289]	flerovium 114 Fl [289]	moscovium 115 Mc [290]	livermorium 116 Lv [293]	tennessine 117 Ts [294]	oganesson 118 Og [294]	
	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.05	lutetium 71 Lu 174.97				
	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]	lawrencium 103 Lr [262]				

Fig. 1 Periodic table of binary metal thiocyanates. The colours highlight whether: a metal binary thiocyanate is known with a determined structure (green), the composition has been reported (blue) or there are no reports of a binary structure or where all reports have been disprove (salmon). Elements excluded from this study (non-metals and radioactive elements) are in grey.

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 3).^{16–19}

The difference in bonding between termini can also be seen in the metal and thiocyanate bond angle: the experimental M-NCS angle distribution peaks at 180° and the M-SCN angle distribution centres on around 100°¹⁶, due to the shapes of the frontier orbitals. The bent M-SCN angle, together with the rod-like shape of thiocyanate means that the symmetries of metal thiocyanates are typically lower than of equivalent halides. This desymmetrization means that the structures are well-ordered, aside from highly ionic salts, in contrast to unlike CN⁻ where the pseudosymmetry produces extensive disorder.²⁰ The head-tail order also offers

new routes for polymorphism (e.g. 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.²¹

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.^{22,23} The strong optical absorption has been harnessed for non-linear optical function,²⁴ and photoconductivity.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)₄. This arises because the large distances between ions produces weak magnetic superexchange and well isolated ions,²⁶ however, long-range magnetic order has been found over comparable distances in Cr[Bi(SCN)₆]₂²⁷ and even CoHg(NCS)₄ has surprisingly complex magnetism.²⁸ Recent work has shown that metal thiocyanates possess a range of interesting magnetic behaviours, including magnetic order at liquid

N \ S	S				
	0	1	2	3	4
0					Zn ¹ (NCS) ₂
1				Cu(NCS) Ag(NCS)	
2		Sn(NCS) ₂			Ni(NCS) ₂ Cd(NCS) ₂
3				Na(NCS) Sb(NCS) ₃ Bi ¹ (NCS) ₃	Bi ² (NCS) ₃
4	Zn ² (NCS) ₂		Hg(NCS) ₂		K(NCS) Cs(NCS) Ba(NCS) ₂

Fig. 2 Metal coordination numbers in the known binary metal thiocyanate structure types. Where the coordination number could be reasonably larger or smaller, the larger coordination number has been chosen. For structures with sites with different metal coordination numbers, both coordination geometries are listed as M(NCSⁿ)_x.

nitrogen temperatures²⁹ and low dimensional magnetism^{29–32}. 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).^{33,34} Thiocyanate compounds are also now being explored as catalysts for a range of reactions, including organophosphate hydrolysis and water photo-oxidation.³⁵ 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 NiI₂ structure-type in halide (Section 2.1); 3D framework structures with eight-coordinate metals with highly distorted CaF₂-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 Tl⁺ (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 and with some variation, Hg and Cu²⁺ (Fig. 3).^{29,30,36–40} This structure is analogous to the CdI₂ structure type common for metal halides,⁴¹ comprising layers of edge-sharing MN₂S₄ oc-

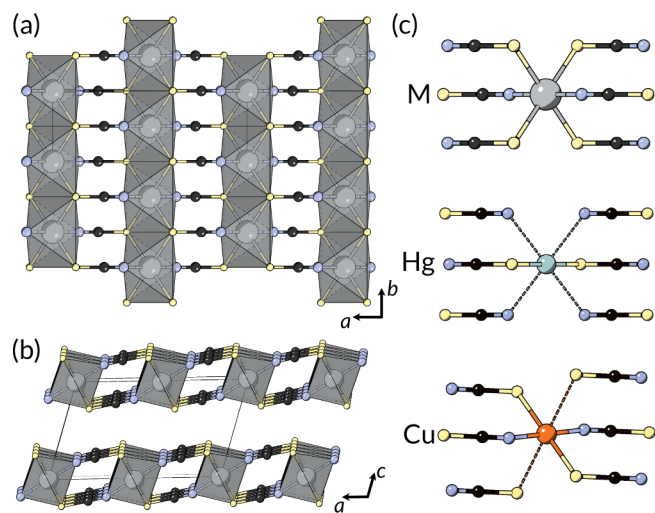


Fig. 3 Structures of the transition metal thiocyanates (M=Ni, Co, Fe, Mn, Hg and Cu) (a) a single *ab* layer, (b) stacking sequence viewed along the *b* layer. (c) Local coordination environment for M = Ni, Co, Mn, Fe; Hg and Cu. Long bonds are shown by dashed lines.

tahedra. 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°, and the M-NCS angle is roughly 160°. 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 HgS₂N₄ pseudo-octahedral coordination, or nearly linear HgS₂ coordination. Cu(II) thiocyanate has a pronounced Jahn-Teller distortion which lengthens one set of Cu-S bonds, lowering the symmetry to *P1̄* 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(BF₄)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.^{30,42–44} 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.²⁹ Thermogravimetric analysis suggests that these compounds are thermally stable in inert atmosphere up to approximately 300°C,²⁹ though Hg(NCS)₂ has long been known for its notable for its spectacular thermal decomposition in air to carbonitrides and mercury sulfides and oxides, the so-called ‘Pharaoh’s Serpent’ reaction.^{45,46}

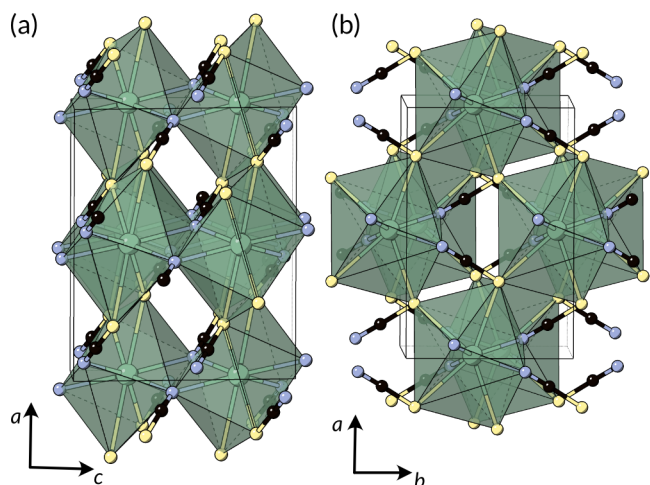


Fig. 4 $\text{Ba}(\text{NCS})_2$ structure type viewed along the (a) b and (b) c directions, adopted for $\text{M}(\text{NCS})_2$ where $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$ and Eu .

These frameworks are also the only characterized binary thiocyanates containing paramagnetic ions (there are no magnetic measurements of $\text{Eu}(\text{NCS})_2$). The first property measurements of $\text{Mn}(\text{NCS})_2$, $\text{Ni}(\text{NCS})_2$ and $\text{Co}(\text{NCS})_2$ included magnetic susceptibility measurements over limited temperature range, which indicated significant antiferromagnetic interactions.⁴⁷ These initial measurements were built upon, and long-range antiferromagnetic order has now been found in $\text{Ni}(\text{NCS})_2$ ³², $\text{Co}(\text{NCS})_2$ ³⁷, $\text{Cu}(\text{NCS})_2$,³⁰ $\text{Mn}(\text{NCS})_2$ ^{29,38} and $\text{Fe}(\text{NCS})_2$.²⁹ Subsequent neutron diffraction revealed unusual layered antiferromagnetism in $\text{Ni}(\text{NCS})_2$,²⁹ and density functional theory calculations suggest that these materials, like the analogous metal halides, may be delaminated to produce 2D magnets.⁴⁸ 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). $\text{Hg}(\text{NCS})_2$ has been reported to form,⁴⁹ as has $\text{Fe}(\text{NCS})_3$,^{50,51} though nothing beyond their apparent composition is known. This family has series of unusual pharmacological functions, acting as both poacher and gamekeeper: $\text{Co}(\text{NCS})_2$ can be used as a test for the presence of cocaine,⁵² and $\text{Cu}(\text{NCS})_2$ is a component in salts designed to obscure the presence of the drug.^{53,54}

2.2 $\text{Ba}(\text{NCS})_2$

The second most common structure type is the 3D $\text{Ba}(\text{NCS})_2$ structure which forms for the alkaline earths Ca, Sr, Ba, and other large divalent cations such as Pb and Eu (Fig. 4).^{55–57} 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. $\text{Ba}(\text{NCS})_2$,

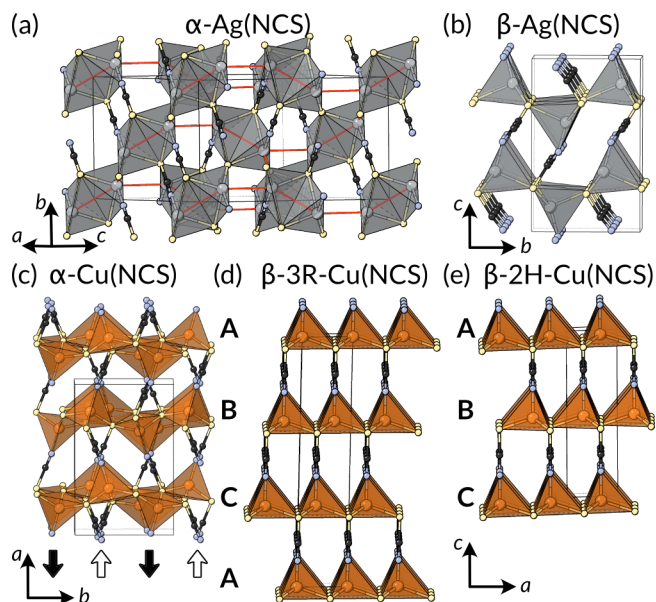


Fig. 5 Structures of the polymorphic Ag(I) and Cu(I) thiocyanates. Structure of (a) $\alpha\text{-Ag}(\text{NCS})$ containing Ag_2 dimers and (b) $\beta\text{-Ag}(\text{NCS})$. Argentophilic interactions highlighted by red lines. Structures of (c) $\alpha\text{-Cu}(\text{NCS})$, (d) $\beta\text{-3R-Cu}(\text{NCS})$ and (e) its polytype $\beta\text{-2H-Cu}(\text{NCS})$.

$\text{Ca}(\text{NCS})_2$ and $\text{Pb}(\text{NCS})_2$ can be formed through dehydration of the readily synthesizable hydrates.^{57,58} $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ is a convenient starting point from any thiocyanate that is synthesized in water due to the insolubility of BaSO_4 . $\text{Eu}(\text{NCS})_2$ is the only known binary thiocyanate containing a paramagnetic ion that does not adopt the $\text{Hg}(\text{NCS})_2$ structure, though its magnetic properties have not been reported. As an isotopic family, Eu(II) can be doped into the other non-fluorescent members hosts to produce materials with green fluorescence at low temperatures.^{59,60}

2.3 Coinage metals

The most polymorphic metal thiocyanates are the monovalent group 10 metals, $\text{Cu}(\text{NCS})$ and $\text{Ag}(\text{NCS})$, which have three and two distinct polymorphs (Fig. 5). $\text{Cu}(\text{NCS})$ 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.^{61,62} There are three reported crystal structures: orthorhombic $Pbca$ $\alpha\text{-Cu}(\text{NCS})$ ⁶³, $P6_3mc$ $2\text{H-}\beta\text{-Cu}(\text{NCS})$ and $R3m$ $3\text{R-}\beta\text{-Cu}(\text{NCS})$.⁶⁴ All of these compounds have in common honeycomb-like CuS layers. $2\text{H-}\beta$ and $3\text{R-}\beta$ have thiocyanates all point in the same direction, yielding polar structures, and in the α phase the thiocyanates alternate up and down in a stripe order pattern, producing a non-polar structure. The two distinct β 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. $2\text{H-}\beta$ has AB stacking, analogous to wurzite, and $3\text{R-}\beta$ has ABC stacking, analogous to sphalerite. The various polymorphs 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 $\text{Cu}(\text{NCS})_2(\text{NH}_3)_2$ solutions.^{63,64}

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, ($\alpha_a = 10.5 \text{ MK}^{-1}$, $\alpha_c = -1.2 \text{ MK}^{-1}$).⁶⁵ Indeed, the thermal expansion is considerably smaller than predicted through DFT using the quasiharmonic approximation.⁶⁶ 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.⁶⁷ Cu(NCS) is of particular interest as the extended CuS layers allow for significant electronic delocalization and hence p-type transparent conduction.^{33,34} Cu(NCS) is solution processable and has been explored as a hole transport layer in solar cells.⁶⁸

Ag(NCS) has two reported polymorphs.^{69–71} β -Ag(NCS) has a structure related to that of α -Cu(NCS) and comprises $\text{Ag}_3\text{S}_3\text{N}_1$ tetrahedra connected by thiocyanates into a tetrahedral network, with a honeycomb type AgS layer with alternating up-and-down thiocyanates.⁷⁰ α -Ag(NCS) contains $\text{Ag}_3\text{S}_3\text{N}$ 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 [101] 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.^{71–73} 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.⁷⁰ β -Ag(NCS) is favoured by rapid precipitation, acidification and the presence of gelatine.⁷⁰ 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.⁷¹

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. 6). As metal pseudohalides, they adopt structures similar to the NaCl (Na, Li)^{74,75} and CsCl structures (K, Rb, Tl, Cs).^{80–83} 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), Tl(NCS) and Cs(NCS).^{76–80}

Sodium and lithium thiocyanate both adopt rocksalt-like structures with space group *Pm \bar{c} n*, in which both the N and S termini are bonded to three metal ions, and each metal ion is coordinated

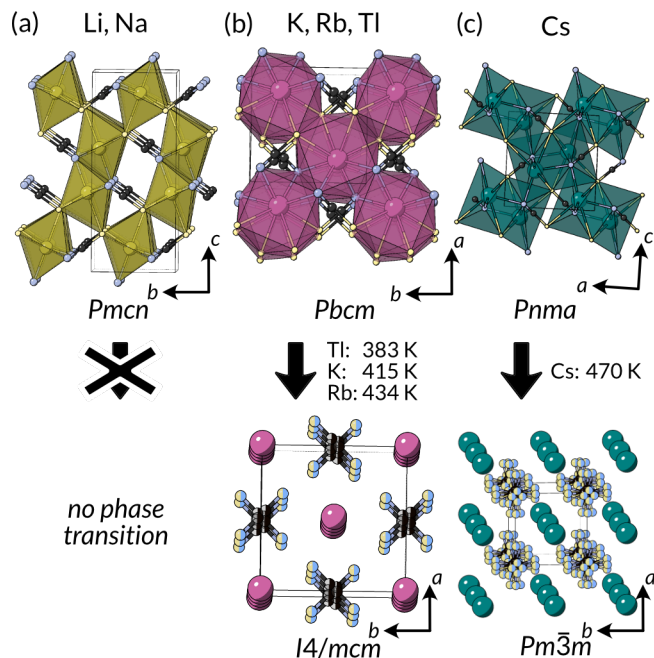


Fig. 6 Structures of the alkali metal and Tl(I) thiocyanates, including their phase transitions. (a) Li(NCS) and Na(NCS) adopt rocksalt derived structures.^{74,75} (b) K(NCS), Rb(NCS) and Tl(NCS) have CsCl-like structures, and undergo phase transition on heating to an anion disordered tetragonal phase.^{76–79} (c) Cs(NCS) has a different CsCl derived structure which transforms into a cubic phase shortly before melting.⁸⁰

by three N and three S atoms.^{74,75} Phase transitions are reported to be absent for Na(NCS) on heating or cooling, or on pressure up to 4 GPa.⁸⁴ Lithium thiocyanate is an Li ion conductor due to the presence of Li vacancies in typically synthesized samples.^{85,86}

K(NCS), Rb(NCS) and Tl(NCS) all adopt the same ordered orthorhombic *Pbcn* structure at room temperature, with eight coordinate NCS, four through the N terminus and four through the S, and eight coordinate metal, both in a distorted cubic coordination.^{81–83} On heating, $T_c = 415 \text{ K}$ for K, 434 K for Rb and 383 K for Tl, a high temperature *I4/m \bar{c} m* tetragonal structure forms, closely related to the low temperature form, but with head-tail NCS disorder.^{77,78,82} The weakly first order transition has been extensively studied for K(NCS)^{76,87} and is well approximated by a pseudospin model.⁸⁸ On compression, a series of additional phases have been reported to exist from thermal analysis and Raman spectroscopy measurements. This suggests that in addition to the room-temperature ambient ordered II phase and high temperature I phase, there are five additional high pressure phases, though there are as yet no diffraction studies confirming their structures.^{84,89}

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 *Pnma* phase and a high temperature maximally symmetric *Pm $\bar{3}$ m* cubic phase, with complete orientational disorder of the NCS^- anion.⁸⁰ The order-disorder transition is first order and the high temperature cubic

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.*⁸²

Na(NCS) and K(NCS) are both readily commercially available. Rb(NCS) and Cs(NCS) can be prepared either by reaction of NH₄(NCS) with M₂(CO₃) in water, or by salt metathesis between M₂(SO₄) and Ba(NCS)₂ and filtering off the insoluble BaSO₄.^{31,82,90} Li(NCS)·H₂O is also commercially available, and the anhydrate can be prepared through careful dehydration.⁷⁵ Although this review focusses on the solid metal thiocyanates, it is worth noting that the low melting points of ionic metal thiocyanates means that they have significant liquid state chemistry as molten salts/ionic liquids.^{84,91,92} Recent reports also suggest that solid solutions of Cu(I) and Zn(II) thiocyanates may also melt, though inhomogeneously.⁹³

2.5 p-block and late transition metals

The remaining binary metal thiocyanates, Sn(NCS)₂,⁹⁴ Bi(NCS)₃,¹⁶ Sb(NCS)₃,⁹⁵ Cd(NCS)₂,^{96,97} and Zn(NCS)₂,⁹⁸ each adopt a unique structures (Fig. 7). Zn(NCS)₂ has a tetrahedrally coordinated Zn, with two distinct sites, one ZnN₄ and the other ZnS₄, and four distinct NCS⁻ anions each of which bridges two Zn atoms.⁹⁸ This leads to a $P\bar{1}$ van der Waals layered structure, analogous to the SiO₂ bilayer.⁹⁹ The first report of the structure of Zn(NCS)₂ refers to it as β -Zn(NCS)₂, which implies the existence of α -Zn(NCS)₂, perhaps of lower symmetry, and although the analogy to SiO₂ suggests polymorphism is feasible, I have found no further details of an alternate phase.

Cd(NCS)₂ crystallizes in $P2_1/c$ and has only a single Cd²⁺ site, octahedrally coordinated by thiocyanate to produce a trans-CdS₄N₂ coordination polyhedron.^{96,97} Every thiocyanate has the S-terminus doubly coordinated, and the N-terminus singly coordinated. Thus far the description of Cd(NCS)₂ is identical to that of Ni(NCS)₂, however in Cd(NCS)₂ there are two distinct NCS⁻ ions, and the overall connectivity of the framework is 3D. The structure is thus analogous to the MnO₂ ramsdellite or Al(OH)O diaspore structure-types.^{100,101}

Sn(NCS)₂ adopts a unique structure and crystallizes in $P\bar{1}$ with a prominent stereochemically active lone pair.⁹⁴ There is a single Sn ion, which is three-coordinate, SnN₂S, with one N-bound terminal NCS⁻, and two bridging NCS⁻ anions. This produces a 1D coordination polymer connected into 2D sheets via weak supramolecular Sn···S interactions, which might be considered 'tetrel-bonds'.¹⁰² The low symmetry of the structure means that the bond lengths vary widely and alternative descriptions are admitted. Sn(NCS)₂ appears to be a promising electron-transport layer for photovoltaic devices^{103,104} Tin(II) thiocyanate crystallizes from aqueous solution of Sn(SO₄) and Na(NCS), whereas Zn(NCS)₂ and Cd(NCS)₂ can be prepared by salt metathesis between the metal sulfate and Ba(NCS)₂ in water.

Bi(NCS)₃ can be synthesized as a orange-yellow crystals through the slow evaporation of aqueous H₃[Bi(SCN)₆] solutions obtained by the acid-base reaction between ethereal HSCN and Bi₂O₂(CO₃).¹⁶ Like Sn(NCS)₂, it also has stereochemically

active metal ions, crystallising in $P\bar{1}$, however it is the most structurally complex of all the reported metal thiocyanate binaries, with two distinct metal ions and six distinct NCS⁻ ions.¹⁶ Both bismuth sites are very distorted, Bi1 has four short bonds, BiN₂S₂, but including longer bonds can be considered to be seven coordinate, BiN₄S₃; Bi2 considering short bonds is a very distorted octahedron, BiN₂S₄, but has an additional short contact to third N atom to make a seven coordinate {BiN_3S_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)₃ can be obtained as colourless crystals by removing THF from the relevant solvate, itself synthesized from the reaction of SbF₃ and trimethylsilyl isothiocyanate.⁹⁵ It crystallizes in the high-symmetry yet polar $I4_1cd$ 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)₃ units. If slightly longer (3.1 Å) Sb-S bonds are considered, the Sb(III) cation has distorted octahedral coordination, SbN₃S₃. 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^{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,³ 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)₂ and Mg(NCS)₂. Beryllium thiocyanate complexes are known,¹⁰⁵ but the solid state

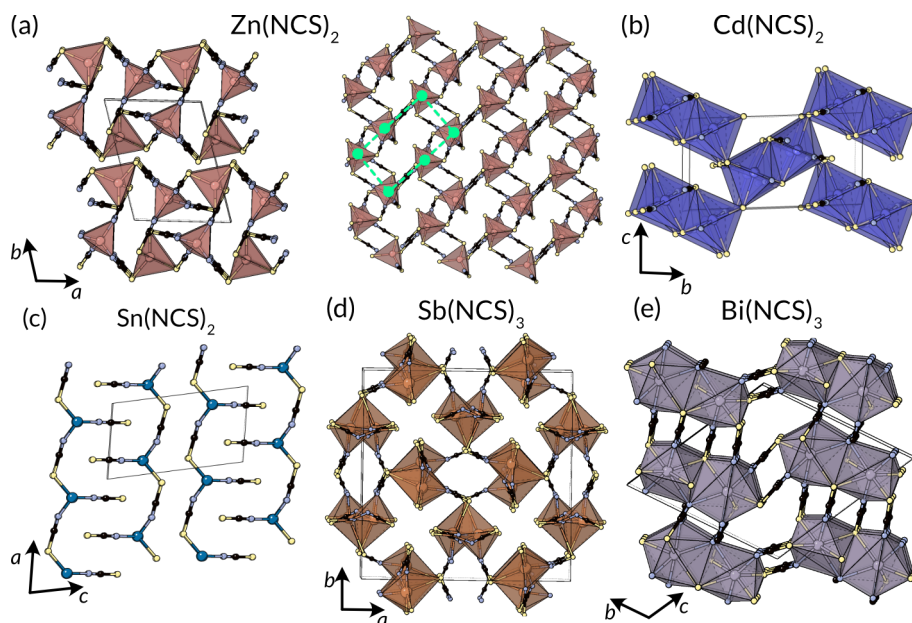


Fig. 7 Structures of p-block and late transition metal thiocyanates. (a) $\text{Zn}(\text{NCS})_2$, viewed along the c direction (left) and normal to the ab layers. 6-rings of the distorted honeycomb shown in bright green. (b) ramsdellite-like $\text{Cd}(\text{NCS})_2$, (c) 1D chain $\text{Sn}(\text{NCS})_2$, (d) $\text{Sb}(\text{NCS})_3$ viewed along the polar c -axis and (e) $\text{Bi}(\text{NCS})_3$ with two symmetry distinct Bi atoms.

preparation has rarely been attempted, and appears to be challenging.¹⁰⁶ $\text{Mg}(\text{NCS})_2 \cdot x\text{H}_2\text{O}$ 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 $\text{Mg}(\text{NCS})_2$ were erroneous.¹⁰⁷ Likewise the oxophilicity of group 3 and lanthanide elements means hydrates are readily formed. Attempts to synthesize $\text{Sc}(\text{NCS})_3$ from solution readily produce solvates of stoichiometry $\text{Sc}(\text{NCS})_3\text{L}_3$, though a poorly characterized ‘yellow scandium trithiocyanate’ has been hinted at.^{108,109} Other group 3 and lanthanide binary thiocyanates are unknown, though many octahedral molecular solvates $\text{Ln}(\text{NCS})_3\text{L}_3$ and homoleptic anionic complexes with N-bound thiocyanate have been reported.^{110,111}

Moving right along the periodic table, the synthesis of $\text{Ti}(\text{NCS})_4$ 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 $\text{Ti}(\text{NCS})_4$ suggests octahedrally coordinated Ti cations with at least some bridging NCS^- anions.¹¹² These data thus imply the structure is more similar to TiF_4 , a 1D structure comprising corner-sharing TiF_6 octahedra,¹¹³ rather than the later halides, TiX_4 , $\text{X} = \text{Cl}, \text{Br}, \text{I}$, which are all tetrahedral molecular materials, with no $\text{Ti}-\text{X}-\text{Ti}$ bridges.^{114–116} There are no reports of $\text{Zr}(\text{NCS})_4$ or $\text{Hf}(\text{NCS})_4$, though the DMF solvates of both are reported.¹¹⁷ 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 $\text{Zr}(\text{NCS})_4$ and $\text{Hf}(\text{NCS})_4$ will have different structures and chemistries.¹¹⁸

All binary group 5 thiocyanates are attested, with the most thoroughly investigated being $\text{V}(\text{NCS})_3$, which can be made through salt metathesis in diethyl ether between NaNCS and VCl_3 , producing a red-brown powder¹¹⁹. $\text{V}(\text{II})$ and $\text{V}(\text{IV})$ thiocyanate complexes are also stable, though only solvates have

been reported.^{120,121} $\text{Nb}(\text{NCS})_5$ and $\text{Ta}(\text{NCS})_5$ are reported to be dimers on the basis of IR spectroscopy, and were prepared by desolvation of the acetonitrile solvates.¹²²

Group 6 binary thiocyanates are less well understood. $\text{Cr}(\text{NCS})_2\text{L}_2$ is well known for a range of solvents, but the an-solvate has not proved possible to prepare, likely in part due to the high sensitivity of $\text{Cr}(\text{II})$ to oxidation.^{37,123} $\text{Cr}(\text{NCS})_3$ is reported to be a deliquescent dark green powder, though characterization is scant.¹⁵ A variety of solvated $\text{Mo}(\text{V})$ and $\text{W}(\text{VI})$ thiocyanates can be made through the reaction of $\text{K}(\text{NCS})$ or $\text{Na}(\text{NCS})$ with MoCl_5 and WCl_6 in organic solvents forming dark red (Mo) or dark brown (W) crystals, but desolvation was not possible by applying a vacuum.¹²⁴ Oxothiocyanato metal complexes are common in these high oxidation states,^{125–127} 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.^{128–130} DFT investigations of the binary $\text{Mo}(\text{NCS})_2$ and $\text{W}(\text{NCS})_2$ suggest they are stable and adopt layered structures, analogous to the $\text{Hg}(\text{NCS})_2$ structure, though with trigonal prismatic metal coordination and metal-metal bonding.¹³¹ The computational stability of these hypothetical layered structures relative to cluster structures, e.g. a $\text{M}_6(\text{NCS})_{12}$ hexametallal cluster, is not reported, despite these being the stable structures of the analogous halides.¹³²

The 3d late transition metals all form divalent binary thiocyanates with the $\text{Ni}(\text{NCS})_2$ structure, as described above, though other oxidation states are unknown except for hints of $\text{Fe}(\text{NCS})_3$ ^{51,133}. 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,^{134,135} but there are no reports of the binary compounds aside brief discussion of an orange-red solid complex

formed on reaction of ReO_4 with KNCS and SnCl_2 , of probably composition $\text{Re}(\text{NCS})_4$ or $\text{ReO}(\text{NCS})_4$.^{136,137}

$\text{Rh}(\text{NCS})_2$ is reported to be a brown powder formed by the reaction of $\text{Rh}_2(\text{CCl}_3\text{COO}_2)_4$ 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 $\text{Rh}(\text{NCS})_3$ and $\text{Ru}(\text{NCS})_3$ as orange-red (Rh) and dark brown (Ru) powders from the salt metathesis in acetonitrile between $\text{K}(\text{NCS})$ and the metal trihalide has been reported.^{139,140} There are no reports of the synthesis of binary $\text{Os}(\text{NCS})_x$ or $\text{Ir}(\text{NCS})_x$ though both are likely to be stable in the +3 oxidation state as implied by the existence of molecular $[\text{M}(\text{NCS})_6]^{3-}$ anions^{141,142} I note that $\text{Os}(\text{NCS})_3$ is likely to be the best candidate for a magnetic ReO_3 -structured metal thiocyanate as it has the most extensive linkage isomerism with thiocyanate of any paramagnetic metal.¹⁴³

$\text{Pd}(\text{NCS})_2$, $\text{Pt}(\text{NCS})_2$ and $\text{Au}(\text{NCS})$ have all been reported and chemical elemental analysis suggests they are pure phase compounds. $\text{Pd}(\text{NCS})_2$ and $\text{Pt}(\text{NCS})_2$ are reported from the thermal decomposition of $\text{M}(\text{NCS})_2(\text{NH}_3)_2$.^{144,145} Aurous thiocyanate has also been reported to form as a white powder of by thermal decomposition of the organometallic complex $[\text{Et}_2\text{Au}(\text{NCS})]_2$ through addition to hot xylene (125°C). Warning: the decomposition of the solid $[\text{Et}_2\text{Au}(\text{NCS})]_2$ at temperatures above 80°C is reported to be explosive.¹⁴⁶ $\text{Au}(\text{NCS})_3$ has been reported to form from the reaction of excess AuCl_3 with soluble alkali metal thiocyanate salts, though further detail of the synthesis and characterization is unreported.¹⁵

The only crystal structure of a group 13 binary thiocyanate is $\text{Tl}(\text{NCS})$, however many more should exist. A number of routes for the synthesis of $\text{In}(\text{NCS})_3$ have been reported: salt metathesis in ethanol between $\text{Na}(\text{NCS})$ and InCl_3 ; metathesis in water between $\text{Ba}(\text{NCS})_2$ and $\text{In}_2(\text{SO}_4)_3$; reaction between In metal and $\text{Hg}(\text{NCS})_2$ and sulfuration of $\text{In}(\text{CN}_3)$.^{147,148} Analysis of X-ray powder diffraction measurements suggests cubic cell of 12 \AA , which implies a ReO_3 -type model consisting of alternating InN_6 and InS_6 octahedra, though there is no atomistic structural model or quantitative refinement of the diffraction data.¹⁴⁷ This structure would be related to the observed $\text{CsCd}(\text{NCS})_3$ structure (Section 3.1).¹⁴⁷ An analogous route to create $\text{Ga}(\text{NCS})_3$, that is the aqueous metathesis reaction between $\text{Ba}(\text{NCS})_2$ and $\text{Ga}_2(\text{SO}_4)_3$, produced a hydrate with N-bound thiocyanate which could not be further dehydrated.¹⁴⁹ The formation of a stable N-bound thiocyanate hydrate is also reported for aluminium, though again desolvation was not possible.¹⁵⁰ The potential for $\text{Tl}(\text{III})$ or $\text{In}(\text{I})$ thiocyanates has not been extensively explored, though the aqueous reaction of TlCl_3 with KNCS has been reported to oxidize NCS^- to HCN and H_2SO_4 .¹⁵¹

In addition to the well-known $\text{Pb}(\text{NCS})_2$ and $\text{Sn}(\text{NCS})_2$, group 14 metal thiocyanates with +4 oxidation state should be feasible. $\text{Sn}(\text{NCS})_4$ is reported to form from the reaction of thiocyanogen $(\text{NCS})_2$ and $\text{Sn}(\text{OH})_4$ in ethereal solution,¹⁵² 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, $\text{A}_x\text{M}_y(\text{NCS})_z$, 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 MN_n and MS_n polyhedra. This means most of these materials use two different framework-forming metal ions: a harder metal for the MN_n polyhedron, and a softer metal for the MS_n polyhedron.

The perovskitoid structures comprise corner-sharing octahedra linked by a single $\mu_{1,1}$ coordinated thiocyanate potentially with cations contained within the pseudocubic cavity (Fig. 8). Like the non-molecular perovskitoid analogues, these metal thiocyanates are an 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 MS_6 cation: $\text{A}_x\text{M}[\text{Bi}(\text{SCN}_6)_y]$,^{16,154,155} $\text{A}_x\text{M}[\text{Pt}(\text{SCN})_6]$ ¹⁹⁷ and $\text{A}_x\text{M}[\text{Cd}(\text{SCN})_6]$ ^{153,156,157}. The occupancy of A site cation varies from $x = 0$, (i.e. an ReO_3 or Prussian Blue type structure¹⁵⁸), to $x = 2$, the standard perovskite stoichiometry.

The very first known perovskitoids were $\text{M}[\text{Pt}(\text{SCN})_6]$, $\text{M} = \text{Fe}$, Cu , Co , reported by Buckton in 1856,¹⁹ 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 $\text{M} = \text{Mn}$ and Ni ,³⁵. 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 $[\text{Pt}(\text{SCN})_6]^{4-}$ compounds. In addition to the perovskitoid structured compounds, Buckton also reported $\text{K}_2[\text{Pt}(\text{SCN})_6]$ (Buckton's salt), now partially structurally determined (Section 3.6),¹⁵⁹ and otherwise unknown compounds of $[\text{Pt}(\text{SCN})_6]^{4-}$ with Hg , Ag , Pb and Au . Other platinum-based perovskitoids are very likely feasible.¹⁶⁰

The first metal thiocyanate perovskitoid to have its structure

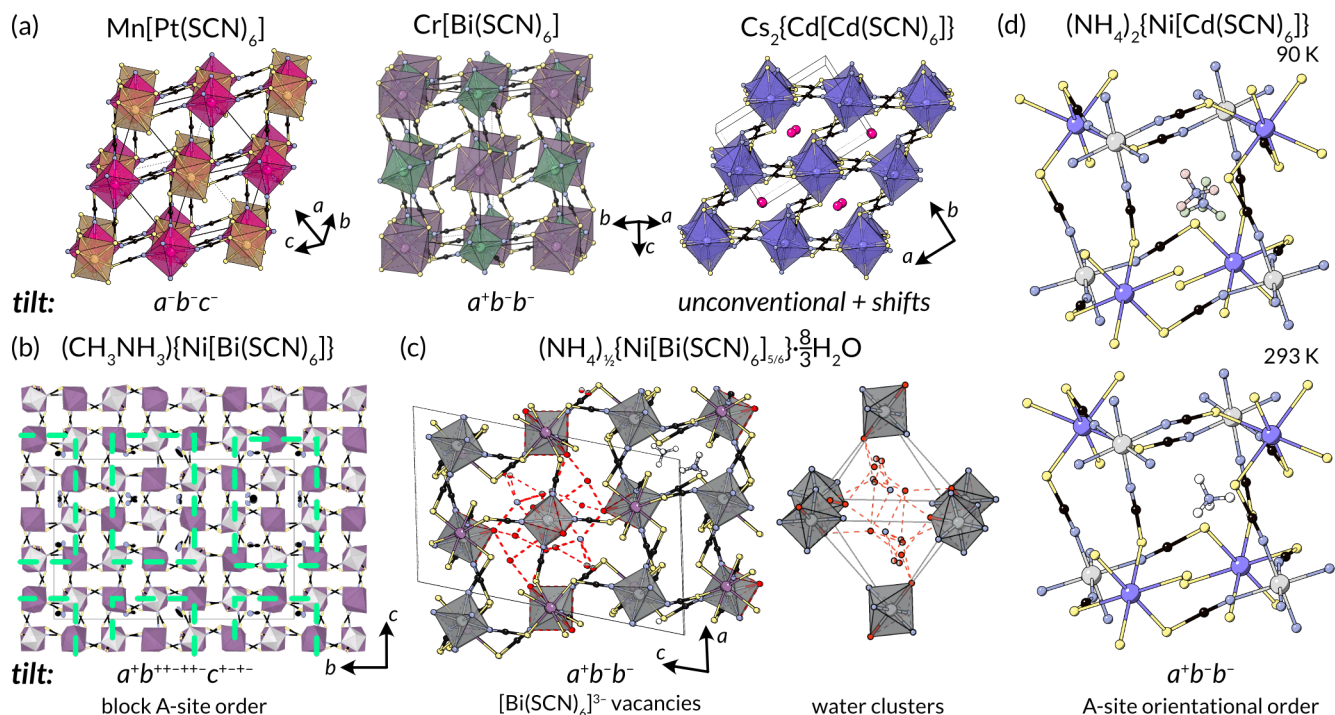


Fig. 8 Structures of perovskitoid thiocyanates $A_x[M[M'(SCN)_6]]$, all with rock-salt M site order. (a) The three classes of perovskite, with $M = Pt^{4+}, Bi^{3+}$ and Cd^{2+} .^{16,35,153} (b) Complex A-site cation order in $(CH_3NH_3)\{Ni[Bi(SCN)_6]\}$.¹⁵⁴ (c) Ordered $[Bi(SCN)_6]^{3-}$ in $(NH_4)_{1/2}\{Ni[Bi(SCN)_6]_{5/6}\} \cdot \frac{8}{3}H_2O$.¹⁵⁵ (d) A-site cation orientational order transition in $(NH_4)_2\{Ni[Cd(SCN)_6]\}$.¹⁵⁶

determined was $CsCd(NCS)_3$ and it is unusual. Rather than having distinct hard and soft cations on the MN_6 and MS_6 sites, it has Cd ions on both. The Cs^+ cation reside in the pores of the anion framework.¹⁵³ Larger cations can also be incorporated within this framework, as shown by $[(CH_3)_3S]_2\{Cd[Cd(SCN)_6]\}$.¹⁵⁷ Cadmium thiocyanate perovskitoids can also occur with mixed metals, where the MN_6 site is occupied by a harder first-row transition metal, including $A_2\{Ni[Cd(SCN)_6]\}$ $A = K, NH_4, (CH_3)_2NH_2$ and $[(CH_3)_2NH_2]_2\{Mn[Cd(SCN)_6]\}$.^{156,157}

The use of $Cr[Bi(SCN)_6]$ 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 $Sc[Bi(SCN)_6]$ and $Fe[Bi(SCN)_6]$.¹⁶ Other bismuth-based perovskitoids containing divalent transition metals and A site cations are now known, including both $A\{Ni[Bi(SCN)_6]\}$, $A = K, NH_4$ and CH_3NH_3 , and more complex stoichiometries: $C(NH_2)_3\{Ni[Bi(SCN)_6]_{5/6}\}$, $Mn_2Bi(NCS)_7 \cdot 7H_2O$, $Co_9Bi_6(NCS)_{36} \cdot 38H_2O$, $M_6Bi_5(NCS)_{30} \cdot 16H_2O \cdot 3NH_4$ $M = Ni, Co$.^{154,155}

As perovskitoids, multiple orderings lowering the symmetry from the $Pm\bar{3}m$ naturally arise. Rocksalt 'M' site order is strongly enforced in all known NCS perovskitoids, due to the preference for MS_6 and 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 $a^+a^+a^+$, $a^+b^+c^+$, $a^-a^-a^-$, $a^-b^-c^-$, $a^+b^-b^-$, $a^+a^+c^-$.^{162,163} Of these, the $M[Pt(SCN)_6]$ perovskitoids adopt the $a^-b^-c^-$ sequence and most

$M[Bi(SCN)_6]$ and $M[Cd(SCN)_6]$ compounds adopt the $a^+b^-b^-$ sequence.¹⁶ As the sulfur bond angle guarantees a tilted structure, larger cations (e.g. molecular cations) induce complex tilts, e.g. $CH_3NH_3\{Ni[Bi(SCN)_6]\}$ adopts the $a^+b^+++++-c^+---$ tilt, or cation vacancies, e.g. $C(NH_2)_3\{Ni[Bi(SCN)_6]_{5/6}\}$ to accommodate them.¹⁵⁴ The greater coordinative flexibility of perovskites with $Cd(NCS)_6$ or $Mn(NCS)_6$ octahedra, allows for unconventional tilts and columnar shifts (a degree of freedom impossible in non-molecular perovskites),^{164–166} particular in the presence of larger cations, whether molecular or Cs^+ .^{153,157} $(CH_3)_3S^+$ 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 $CsNiCl_3$ -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 frameworks¹⁵⁴, but an order-disorder phase transition has been found in $(NH_4)_2\{Ni[Cd(SCN)_6]\}$,¹⁵⁶ and A-sites are often disordered 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 diamondoid net, comprising alternating MN_4 and MS_4 tetrahedra (Fig. 9). This structure type

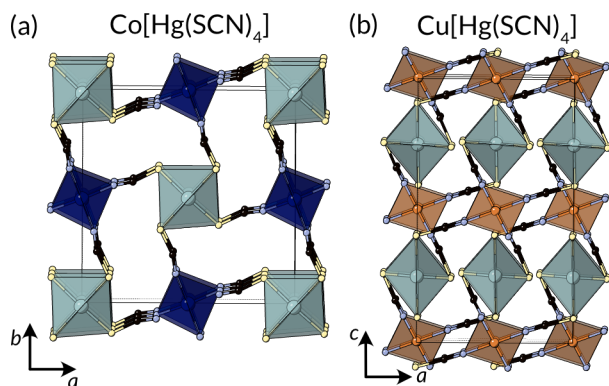


Fig. 9 Structures of (a) diamondoid $\text{Co}[\text{Hg}(\text{SCN})_4]$ and (b) the related $\text{Cu}[\text{Hg}(\text{SCN})_4]$.

was first determined by Jeffery for $\text{CoHg}(\text{SCN})_4$,¹⁷ historically widely used in microanalysis¹⁷⁰ and as a calibrant for measures of magnetic susceptibility,²⁶ though there is both a significant easy-plane zero field splitting, with $D = +10.6(5) \text{ cm}^{-1}$, and weak superexchange $\tau J = -0.2(1) \text{ cm}^{-1}$.²⁸ As this family crystallizes in the polar $I\bar{4}$ space group, these compounds are also of interest for their non-linear optical properties, particularly $\text{ZnHg}(\text{SCN})_4$,¹⁷¹ $\text{MnHg}(\text{SCN})_4$ and $\text{FeHg}(\text{SCN})_4$.¹⁷²

The structure is now known for $\text{M}[\text{Hg}(\text{SCN})_4]$ for $\text{M} = \text{Zn}$,¹⁷¹ Co ,¹⁷ Fe ,¹⁷² Mn ,¹⁷² Cd ;¹⁷³ and $\text{Zn}[\text{Cd}(\text{SCN})_4]$.^{174,175} $\text{Cu}[\text{Hg}(\text{SCN})_4]$ adopts a related but distinct structure containing square planar $\text{Cu}(\text{NCS})_4$ ions, which has two subtly different monoclinic and orthorhombic polymorphs.^{176,177} $\text{Ni}[\text{Hg}(\text{SCN})_4]$ is not known, with hydrates and methanlates forming instead (likely due to the difficulty of preparing tetrahedral $\text{Ni}(\text{II})$).¹⁷⁸ The crystal structure of a related composition, $\text{NiHg}_2(\text{SCN})_6$, has been reported but the unphysical NiN_6 coordination sphere, with N–N distances as short as 1.64 \AA , and N–Ni–N angles of 50° suggests the structure is incorrect.¹⁷⁹ The true structure may be related to the complex structure of $\text{MnHg}_2(\text{SCN})_6$ (Section 3.4).¹⁸⁰

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 often be made (Fig. 10). $\text{Zn}_3\text{Bi}_2\text{NCS}_6$ 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 database¹⁸¹. $\alpha\text{-Zn}_3\text{Bi}_2\text{NCS}_6$ is of particular interest as it can be thought of as comprising $\text{Zn}[\text{Bi}(\text{SCN})_4]$ -perovskite type layers, with every other layer containing an additional Zn_2^+ cation connecting them.¹⁵⁵

$\text{Zn}[\text{Ag}_2(\text{SCN})_4]$ 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 $\text{Cu}(\text{NCS})$.^{182,183}

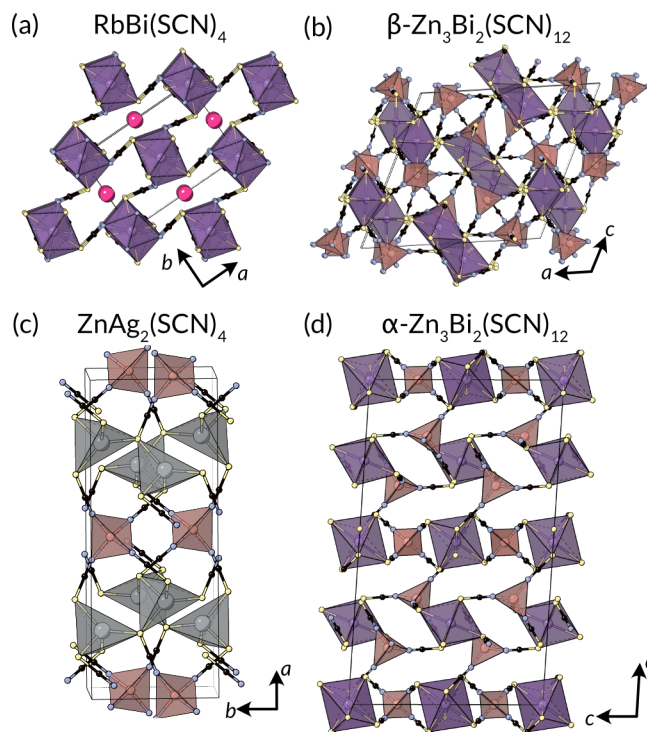


Fig. 10 Structures of 3D ternaries. (a) $\text{Rb}[\text{Bi}(\text{SCN})_4]$ has an anionic $[\text{Bi}(\text{SCN})_4]^-$ framework, (b) $\beta\text{-Zn}_3\text{Bi}_2\text{NCS}_6$ is assembled from BiS_6 and ZnN_4 polyhedra. (c) $\text{ZnAg}_2(\text{SCN})_4$ comprises ZnN_4 and AgS_4 tetrahedra with 3-coordinate S. (d) $\alpha\text{-Zn}_3\text{Bi}_2\text{NCS}_6$ consists of $\text{ZnBi}(\text{SCN})_4$ perovskite layers connected by $\text{Zn}(\text{NCS})_4$ tetrahedra.

$\text{RbBi}(\text{SCN})_4$ structure is related to both the perovskite and post-perovskite structures, with edge-sharing chains, corner-sharing in the perpendicular directions to form a 3D network. The Rb^+ cations sit within the pores of this structure.¹⁸⁴ Literature reports make clear that many more 3D ternary thiocyanate frameworks, are feasible.^{94,185–191}

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 $\text{Rb}[\text{Cd}(\text{SCN})_3]$,¹⁵³ and later expanded to $\text{Cs}[\text{M}(\text{NCS})_3]$, where $\text{M} = \text{Ni}, \text{Co}$,

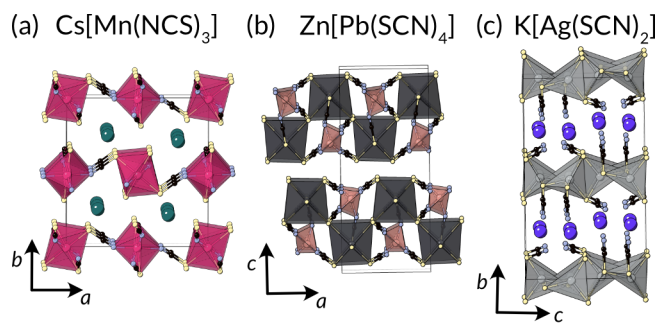


Fig. 11 Structures of the layered ternary metal thiocyanates. (a) Post-perovskite $\text{Cs}[\text{Mn}(\text{NCS})_3]$, (b) $\text{Zn}[\text{Pb}(\text{SCN})_4]$ with its (110) block perovskite structures and (c) $\text{K}[\text{Ag}(\text{SCN})_2]$ formed from edge- and corner-sharing AgS_4 tetrahedra.

Mn.^{31,192} These materials, like the perovskites, are formed from two different metal coordination environments, but in this case they are MS_2N_4 and MS_4N_2 . These polyhedra edge-share through the length of the NCS^- ligand with polyhedra of the same kind and corner-share with the others, to form anionic sheets of composition $[M(NCS)_3]^-$, with the counter-cation lying between them. The post-perovskite oxides and halides are typically formed at GPa to 100 GPa pressures, e.g. $MgSiO_3$,^{193,194} $CaIrO_3$ ¹⁹⁵ and $NaMF_3$ ($M = Mg, Zn, Ni, Co, Fe$)^{196–200}, and so the relative accessibility of thiocyanate post-perovskites has allowed for more detailed investigation of their magnetism.³¹

$Pb[Zn(NCS)_4]$ comprises $Pb(SCN)_6$ octahedra and $Zn(NCS)_4$ tetrahedra, both significantly distorted and connected into neutral layers.¹⁸ Unlike the other discussed ternaries thus far, there are direct $Pb-S-Pb$ connections in this structure and the PbS_2 substructure thus resembles a 2D perovskite with $\{110\}$ type layers, e.g. the MnF_2 substructure in $BaMnF_4$.²⁰¹

$MnHg_2(SCN)_6$ has a large number of distinct metal environments, with four different Hg sites and two different Mn sites.¹⁸⁰ All Hg atoms form part of $Hg_2(SCN)_6$ dimers of tetrahedra, with one dimer consisting of edge-sharing $Hg(SCN)_4$ tetrahedra linked through the S atoms, and the other containing one $Hg(SCN)_4$ tetrahedron and one $Hg(NCS)(SCN)_3$ 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_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_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_2 dimer are aligned along the a -axis and hence only have half the inter-chain connections due to their reduced coordination numbers. The layer structure can therefore be related to the $M(NCS)_3$ layer found post-perovskite structure, though with considerable additional structural complexity.

$K[Ag(SCN)_2]$ is formed from AgS_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^- anions point into the interlayer gallery towards the K atoms.^{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). $Rb_2[Ag(SCN)_3]$ comprises a 1D chain of corner-sharing AgS_4 tetrahedra.²⁰⁴ Similarly, $Rb[Hg(SCN)_3]$ consists of chain of corner sharing HgS_4 tetrahedra connected through the S-atom of the NCS^- ligand.¹⁵³ $Cs[Hg(SCN)_3]$ also has a chain structure of tetrahedra, but in this case, the tetrahedra edge-share through S to form $Hg_2S_6N_2$ dimers, which are connected through the length of thiocyanate to form extended 1D connectivity.¹⁵³

The isostructural family $M[Au(SCN)_2]$ $M = K, Rb, Cs$, have an very different kind of chain structure, comprising linearly coordinated Au(I) anions $[Au(SCN)_2]^-$ stacked and connected by

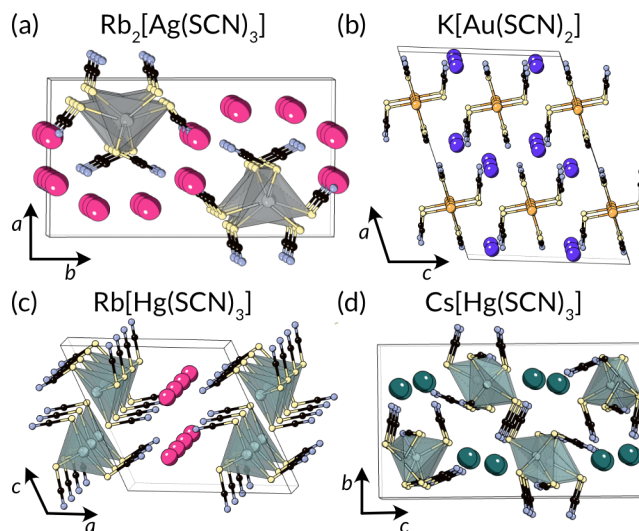


Fig. 12 Structures of 1D ternary metal thiocyanates. (a) $Rb_2[Ag(SCN)_3]$ comprising chains of corner sharing AgS_4 tetrahedra, (b) $K[Au(SCN)_2]$ consists of $[Au(SCN)_2]^-$ anions connected through strong aurophilic interactions, (c) $Rb[Hg(SCN)_3]$ also consists of chains of corner-sharing HgS_4 tetrahedra and (d) $Cs[Hg(SCN)_3]$ contains edge-sharing dimerized tetrahedra connected through a $Hg-NCS-Hg$ linkage.

aurophilic interactions, with a slight alternation of Au-Au distance e.g. for $K[Au(SCN)_2]$ $d_{Au-Au} = 3.04$ & 3.00 Å.²⁰⁵ Different M cations lead to slightly different d_{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 homoleptic metal thiocyanate complexes are probably the most diverse family of metal thiocyanate compounds, but reported crystal structures typically include organic counteranions or solvent.^{3,111,212} 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, $Cs_2[Ag(SCN)_3]$ and $K_2[Ag(SCN)_3]$, comprising edge-sharing AgS_4 tetrahedra, stabilized by intradimer argentophilic interactions ($d_{Ag-Ag} = 3.3$ Å).^{202,204}

The most diverse class of salts contain octahedrally coordinated metals, i.e. $[M(NCS)_x(SCN)_{6-x}]^{y-}$ anions, for which crystal structures exist for y from 2 to 4, and for $x = 0$ or 6, other values are reported with organic cations and solvates. $Na_4[Mg(NCS)_6]$ has a trigonal structure, $P\bar{3}1c$, built from two kinds of layers, the first composed of alternating $[Mg(NCS)_6]^{4-}$ and Na^+ cations and the second containing just Na^+ cations.²⁰⁸ $Cs_3[Mo(NCS)_6]$ is hexagonal, with columns of $[Mo(NCS)_6]^{3-}$ anions with Cs^+ cations in between. The crystal structure shows very significant disorder which remains present down to 115 K.²¹³ $K_3[Rh(SCN)_6]$, despite the compositional similarity adopts a different structure

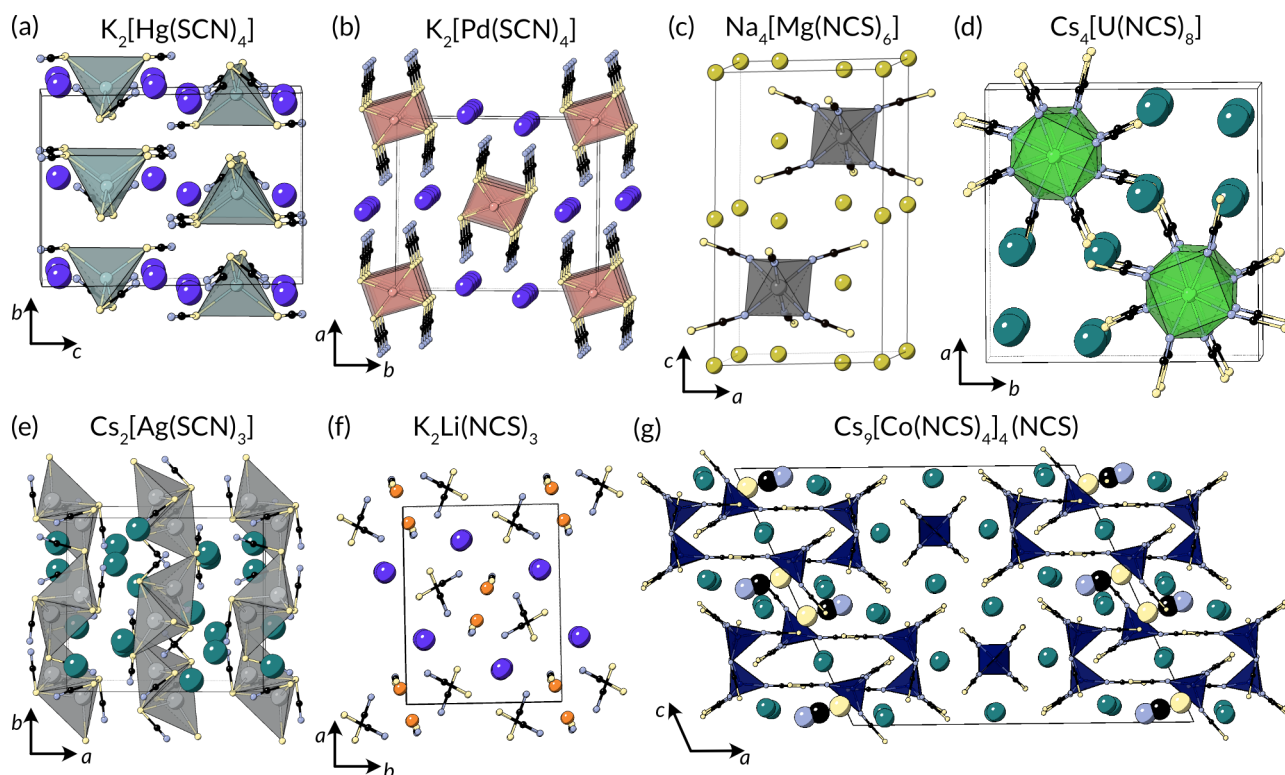


Fig. 13 Structures of metal thiocyanate salts. Example of salts with each kind of local geometry are shown: (a) tetrahedral $K_2[Hg(SCN)_4]$,²⁰⁶ (b) square planar $K_2[Pd(SCN)_4]$,²⁰⁷ (c) octahedral, $Na_4[Mg(NCS)_6]$,²⁰⁸ (d) square antiprismatic $Cs_4[U(NCS)_8]$,²⁰⁹ (e) tetrahedral dimers in $Cs_2[Ag(SCN)_3]$,²⁰⁴ and mixed salts (f) $K_2Li(NCS)_3$,²¹⁰ and $Cs_9[Co(NCS)_4]_4(NCS)$, in which the non-bonded thiocyanate ion has been shown larger for clarity.²¹¹

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 $P\bar{3}m1$.¹⁵⁹ The thiocyanate anions cannot be resolved, but the arrangement of the alkali cations and $[Pt(SCN)_6]^{2-}$ anion is likely an anti- CdI_2 structure type.¹⁵⁹

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 $K_2[Pd(SCN)_4]$ ²⁰⁷ and $K_2[Pt(SCN)_4]$, 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. $Cs_5[Nd(NCS)_8]$ has a NdN_8 coordination geometry intermediate between cubic and square antiprismatic,²¹⁵ whereas $Cs_4[U(NCS)_8]$ has a square antiprismatic UN_8 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. $Cs_9[Co(NCS)_4]_4(NCS)$ contains, in addition to the tetrahedral $[Co(NCS)_4]^{2-}$ anions which stack on top of either other, free NCS^- anions.²¹¹ $K_2Li(NCS)_3$ 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_3S tetrahedra bridged into chains through the length of a NCS^- ligand. Each individual chain is polar and each chain has the same polarity.²¹⁰

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.

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

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 materials datasets recently produced.^{216–218} This perhaps arises from the difficulty current computational approaches have with molecule-containing materials, which are typically metastable 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.²¹⁹ 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)₂, M = Cu, Ni, Co, Fe, Mn, Zn, Hg; ZnPb(NCS)₄ and Mn₂Hg(NCS)₆) and more than half of these have not been previously proposed to be stable as monolayers theoretically.^{216,220–222} 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 understanding.

Conflicts of interest

No conflicts of interest to declare.

Acknowledgements

Joshua Hill, Euan Basseby and Claire Wilkinson are acknowledged for their insightful comments. Xiaoxuan Su, Gabriel Abarca, Jesum Alves Fernandes, Anabel Lanterna and the University of Nottingham Library are thanked for their assistance obtaining difficult to locate articles. M.J.C. acknowledges UKRI funding (EP/X042782/1).

Author Contributions

Notes and references

- 1 L. Birckenbach and K. Kellermann, *Berichte der deutschen chemischen Gesellschaft (A and B Series)*, 1925, **58**, 786–794.
- 2 L. Birckenbach and K. Kellermann, *Berichte der deutschen chemischen Gesellschaft (A and B Series)*, 1925, **58**, 2377–2386.
- 3 A. H. Norbury, in *Advances in Inorganic Chemistry and Radiochemistry*, Elsevier, 1975, vol. 17, pp. 231–386.
- 4 K. Eschliman and S. H. Bossmann, *Synthesis*, 2019, **51**, 1746–1752.
- 5 V. Schulz, *Clinical Pharmacokinetics*, 1984, **9**, 239–251.
- 6 Y. Zhang and P. Talalay, *Cancer Research*, 1994, **54**, 1976s–1981s.
- 7 D. T. Halfen, L. M. Ziurys, S. Brünken, C. A. Gottlieb, M. C. McCarthy and P. Thaddeus, *The Astrophysical Journal*, 2009, **702**, L124.
- 8 R. Porrett, *Philosophical Transactions of the Royal Society of London*, 1814, **104**, 527–556.
- 9 M. E. Weeks, *Journal of Chemical Education*, 1932, **9**, 1915.
- 10 F. Tamadon and K. Seppelt, *Angewandte Chemie International Edition*, 2013, **52**, 767–769.
- 11 D. K. Fujita, B. B. Cunningham and T. C. Parsons, *J. Inorg. Nucl. Chem. Letters*, 1969, **5**, 307–313.
- 12 S. Baran, A. Hoser, M. Rams, S. Ostrovsky, T. Neumann, C. Näther and Z. Tomkowicz, *Journal of Physics and Chemistry of Solids*, 2019, **130**, 290–297.
- 13 T. Neumann, M. Ceglarska, L. S. Germann, M. Rams, R. E. Dinnebier, S. Suckert, I. Jess and C. Näther, *Inorganic Chemistry*, 2018, **57**, 3305–3314.
- 14 A. M. Golub, H. Köhler and V. V. Skopenko, *Chemistry of Pseudohalides*, Elsevier, Amsterdam, 1986, vol. 21.
- 15 H. E. Williams, *Cyanogen Compounds: Their Chemistry, Detection and Estimation*, Edward Arnold & Co, London, 2nd edn., 1948.
- 16 M. J. Cliffe, E. N. Keyzer, M. T. Dunstan, S. Ahmad, M. F. L. De Volder, F. Deschler, A. J. Morris and C. P. Grey, *Chemical Science*, 2019, **10**, 793–801.
- 17 J. W. Jeffery, *Nature*, 1947, **159**, 610–610.
- 18 K. Brodersen, H. Procher and H.-U. Hummel, *Zeitschrift für Naturforschung B*, 1987, **42**, 679–681.
- 19 G. B. Buckton, *Quarterly Journal of the Chemical Society of London*, 1855, 22–43.
- 20 A. Simonov, T. De Baerdemaeker, H. L. B. Boström, M. L. Ríos Gómez, H. J. Gray, D. Chernyshov, A. Bosak, H.-B. Bürgi and A. L. Goodwin, *Nature*, 2020, **578**, 256–260.
- 21 C. Wechwithayakhlung, D. M. Packwood, D. J. Harding and P. Pattanasattayavong, *Journal of Physics and Chemistry of Solids*, 2021, **154**, 110085.
- 22 S. A. Lewin and R. S. Wagner, *Journal of Chemical Education*, 1953, **30**, 445.
- 23 K. C. De Berg, *The Iron(III) Thiocyanate Reaction: Research History and Role in Chemical Analysis*, Springer International Publishing, Cham, 2019.
- 24 D. Yuan, D. Xu, M. Liu, F. Qi, W. Yu, W. Hou, Y. Bing, S. Sun and M. Jiang, *Applied Physics Letters*, 1997, **70**, 544–546.
- 25 B. O'Regan and D. T. Schwartz, *Chemistry of Materials*, 1995, **7**, 1349–1354.
- 26 D. B. Brown, V. H. Crawford, J. W. Hall and W. E. Hatfield, *The Journal of Physical Chemistry*, 1977, **81**, 1303–1306.

- 27 M. J. Cliffe, O. Fabelo and L. Cañadillas-Delgado, *CrystEngComm*, 2022, **24**, 7250–7254.
- 28 D. Nelson and L. W. Ter Haar, *Inorganic Chemistry*, 1993, **32**, 182–188.
- 29 E. N. Bassey, J. A. M. Paddison, E. N. Keyzer, J. Lee, P. Manuel, I. da Silva, S. E. Dutton, C. P. Grey and M. J. Cliffe, *Inorganic Chemistry*, 2020, **59**, 11627–116339.
- 30 M. J. Cliffe, J. Lee, J. A. M. Paddison, S. Schott, P. Mukherjee, M. W. Gaultois, P. Manuel, H. Siringhaus, S. E. Dutton and C. P. Grey, *Physical Review B*, 2018, **97**, 144421.
- 31 M. Geers, J. Y. Lee, S. Ling, O. Fabelo, L. Cañadillas-Delgado and M. J. Cliffe, *Chemical Science*, 2023, **14**, 3531–3540.
- 32 G. C. DeFotis, K. D. Dell, D. J. Krovich and W. W. Brubaker, *Journal of Applied Physics*, 1993, **73**, 5386–5388.
- 33 P. Pattanasattayavong, N. Yaacobi-Gross, K. Zhao, G. O. N. Ndjawa, J. Li, F. Yan, B. C. O'Regan, A. Amassian and T. D. Anthopoulos, *Advanced Materials*, 2013, **25**, 1504–1509.
- 34 J. E. Jaffe, T. C. Kaspar, T. C. Droubay, T. Varga, M. E. Bowden and G. J. Exarhos, *Journal of Physical Chemistry C*, 2010, **114**, 9111–9117.
- 35 H. Tabe, M. Matsushima, R. Tanaka and Y. Yamada, *Dalton Transactions*, 2019, **48**, 17063–17069.
- 36 E. Dubler, A. Relier and H. R. Oswald, *Zeitschrift für Kristallographie*, 1982, **161**, 265–277.
- 37 E. Shurdha, S. H. Lapidus, P. W. Stephens, C. E. Moore, A. L. Rheingold and J. S. Miller, *Inorganic Chemistry*, 2012, **51**, 9655–9665.
- 38 T. Neumann, G. Gallo, R. E. Dinnebier and C. Näther, *Zeitschrift für anorganische und allgemeine Chemie*, 2020, **646**, 88–94.
- 39 A. L. Beauchamp and D. Goutier, *Canadian Journal of Chemistry*, 1972, **50**, 977–981.
- 40 C. D. Flint and M. Goodgame, *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1970, 442–445.
- 41 R. M. Bozorth, *Journal of the American Chemical Society*, 1922, **44**, 2232–2236.
- 42 C. Claus, *Journal für praktische Chemie*, 1838, **XV**, 401–411.
- 43 J. C. Philip and A. Bramley, *Journal of the Chemical Society, Transactions*, 1916, **109**, 597–603.
- 44 J. A. Hunter, W. H. S. Massie, J. Meiklejohn and J. Reid, *Inorganic and Nuclear Chemistry Letters*, 1969, **5**, 1–4.
- 45 H. Irving, *Science Progress (1933-)*, 1935, **30**, 62–66.
- 46 T. S. Miller, A. d'Aleo, T. Suter, A. E. Aliev, A. Sella and P. F. McMillan, *Zeitschrift für anorganische und allgemeine Chemie*, 2017, **643**, 1572–1580.
- 47 D. M. L. Goodgame, *Journal of the Chemical Society (Resumed)*, 1963, 268–274.
- 48 Y. Wu, W. Sun, S. Liu, B. Wang, C. Liu, H. Yin and Z. Cheng, *Nanoscale*, 2021, **13**, 16564–16570.
- 49 K. Huttner and S. Knappe, *Zeitschrift für anorganische und allgemeine Chemie*, 1930, **190**, 27–37.
- 50 Berzelius, J., *Lehrbuch der Chemie*, 1826, **2**, 771.
- 51 H. I. Schlesinger and H. B. van. Valkenburgh, *Journal of the American Chemical Society*, 1931, **53**, 1212–1216.
- 52 R. Haddoub, D. Ferry, P. Marsal and O. Siri, *New Journal of Chemistry*, 2011, **35**, 1351–1354.
- 53 T. Laussmann, I. Grzesiak, A. Krest, K. Stirnat, S. Meier-Giebing, U. Ruschewitz and A. Klein, *Drug Testing and Analysis*, 2015, **7**, 56–64.
- 54 C. P. Krebs, M. T. Costelloe and D. Jenks, *The International Journal on Drug Policy*, 2000, **11**, 351–356.
- 55 C. Wickleder and P. Larsen, *Zeitschrift für Naturforschung B*, 2002, **57**, 1419–1426.
- 56 C. Wickleder, *Zeitschrift Fur Anorganische Und Allgemeine Chemie*, 2001, **627**, 1693.
- 57 J. A. A. Mokuolu and J. C. Speakman, *Acta Crystallographica*, 1975, **B31**, 172–176.
- 58 K. M. Herstein, *Inorganic Syntheses*, 1950, **3**, 24–26.
- 59 C. Wickleder, *Journal of Alloys and Compounds*, 2004, **374**, 10–13.
- 60 C. Wickleder, *Chemistry of Materials*, 2005, **17**, 1228–1233.
- 61 D. C. Buck and L. W. Strock, *American Mineralogist*, 1955, **40**, 192–200.
- 62 A. F. Wright, *Journal of Applied Physics*, 1997, **82**, 5259–5261.
- 63 M. Kabesova, M. Dunaj-Jurco, M. Serator, J. Gazo and J. Garaj, *Inorganica Chimica Acta*, 1976, **17**, 161–165.
- 64 D. L. Smith and V. I. Saunders, *Acta Crystallographica*, 1982, **B38**, 907–9.
- 65 J. Wang, Q. Gao, Y. Gao, Y. Luo, J. Guo, Q. Sun and E. Liang, *Applied Physics Letters*, 2021, **118**, 222105.
- 66 Y. Shen, F. Q. Wang and Q. Wang, *Nano Energy*, 2020, **73**, 104822.
- 67 Z. Yang, B. Wu, C. Zhai, S. Niu, B. Sun, L. Dang, C. Gu, X. Qi, Y. Tian, J. Li, S. Ma and M. Yao, *Inorganic Chemistry*, 2022, **61**, 19274–19281.
- 68 S. Ye, W. Sun, Y. Li, W. Yan, H. Peng, Z. Bian, Z. Liu and C. Huang, *Nano Letters*, 2015, **15**, 3723–3728.
- 69 H.-L. Zhu, G.-F. Liu and F.-J. Meng, *Zeitschrift für Kristallographie - New Crystal Structures*, 2003, **218**, 285–286.
- 70 D. L. Smith, J. E. Maskasky and L. R. Spaulding, *Journal of Applied Crystallography*, 1982, **15**, 488–492.
- 71 D. J. Williams, L. L. Daemen, S. C. Vogel and Th. Proffen, *Journal of Applied Crystallography*, 2007, **40**, 1039–1043.
- 72 A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. O. Evans, D. A. Keen, L. Peters and M. G. Tucker, *Science (New York, N.Y.)*, 2008, **319**, 794–797.
- 73 H. Schmidbaur and A. Schier, *Angewandte Chemie International Edition*, 2015, **54**, 746–784.
- 74 P. H. van Rooyen and J. C. A. Boeyens, *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, 1975, **31**, 2933–2934.
- 75 O. Reckeweg, A. Schulz, B. Blaschkowski, T. Schleid and F. J. DiSalvo, *Zeitschrift für Naturforschung B*, 2014, **69b**, 17–24.
- 76 A. Fuith, *Phase Transitions*, 1997, **62**, 1–93.
- 77 Y. Yamada and T. Watanabé, *Bulletin of the Chemical Society*

- of Japan, 1963, **36**, 1032–1037.
- 78 W. Klement, *Bulletin of the Chemical Society of Japan*, 1976, **49**, 2148–2153.
- 79 O. Blaschko, W. Schwarz, W. Schranz and A. Fuith, *Journal of Physics: Condensed Matter*, 1994, **6**, 3469.
- 80 S. Manolatos, M. Tillinger and B. Post, *Journal of Solid State Chemistry*, 1973, **7**, 31–35.
- 81 H. P. Klug, *Zeitschrift für Kristallographie - Crystalline Materials*, 1933, **85**, 214–222.
- 82 A. Shlyaykher, T. Pippinger, T. Schleid, O. Reckeweg and F. Tambornino, *Zeitschrift für Kristallographie - Crystalline Materials*, 2022, **237**, 69–75.
- 83 R. Lippman and R. Rudman, *The Journal of Chemical Physics*, 1983, **79**, 3457–3461.
- 84 C. W. F. T. Pistorius, J. B. Clark and E. Rapoport, *The Journal of Chemical Physics*, 1968, **48**, 5123–5131.
- 85 M. Joos, M. Conrad, A. Rad, P. Kaghazchi, S. Bette, R. Merkle, R. E. Dinnebier, T. Schleid and J. Maier, *Physical Chemistry Chemical Physics*, 2022, **24**, 20189–20197.
- 86 M. Joos, M. Conrad, I. Moudrakovski, M. W. Terban, A. Rad, P. Kaghazchi, R. Merkle, R. E. Dinnebier, T. Schleid and J. Maier, *Physical Chemistry Chemical Physics*, 2022, **24**, 20198–20209.
- 87 W. Schranz, *Phase Transitions*, 1994, **51**, 1–66.
- 88 W. Schranz, H. Warhanek, R. Blinc and B. Žekš, *Physical Review B*, 1989, **40**, 7141–7149.
- 89 D. M. Adams and M. Pogson, *Journal of Raman Spectroscopy*, 1988, **19**, 321–327.
- 90 S. S. Ti, S. F. A. Kettle and Ø. Ra, *Spectrochimica Acta Part A: Molecular Spectroscopy*, 1976, **32**, 1603–1613.
- 91 D. H. Kerridge, in *Advances in Molten Salt Chemistry: Volume 3*, ed. J. Braunstein, G. Mamantov and G. P. Smith, Springer US, Boston, MA, 1975, pp. 249–273.
- 92 D. H. Kerridge and S. J. Walker, *Journal of Inorganic and Nuclear Chemistry*, 1976, **38**, 1795–1798.
- 93 C. Wechwithayakhlung, S. Wannapai boon, S. Na-Phattalung, P. Narabadeesuphakorn, S. Tanjindaprateep, S. Waiprasoet, T. Imyen, S. Horike and P. Pattanasattayavong, *Inorganic Chemistry*, 2021, **60**, 16149–16159.
- 94 B. R. Chamberlain and W. Moser, *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1969, **0**, 354–358.
- 95 S. Arlt, J. Harloff, A. Schulz, A. Stoffers and A. Villinger, *Inorganic Chemistry*, 2019, **58**, 5305–5313.
- 96 G. Srdanov, R. Herak, B. Prelesnik and M. Jeremic, *Bulletin de la Société Chimique Beograd*, 1979, **44**, 561–565.
- 97 M. Cannas, G. Carta, A. Cristini and G. Marongiu, *Journal of the Chemical Society, Dalton Transactions*, 1976, 300–301.
- 98 L. A. Aslanov, V. M. Ionov and K. Kynev, *Crystallography reports*, 1976, **21**, 1198–1199.
- 99 C. Büchner and M. Heyde, *Progress in Surface Science*, 2017, **92**, 341–374.
- 100 A. M. Byström, E. W. Lund, L. K. Lund and M. Hakala, *Acta Chemica Scandinavica*, 1949, **3**, 163–173.
- 101 F. J. Ewing, *The Journal of Chemical Physics*, 2004, **3**, 203–207.
- 102 C. Wechwithayakhlung, D. M. Packwood, J. Chaopaknam, P. Worakajit, S. Ittisanronnachai, N. Chanlek, V. Promarak, K. Kongpatpanich, D. J. Harding and P. Pattanasattayavong, *Journal of Materials Chemistry C*, 2019, **7**, 3452–3462.
- 103 A. Seikhan, M. Neophytou, M. Kirkus, E. Abou-Hamad, M. N. Hedhili, E. Yengel, Y. Firdaus, H. Faber, Y. Lin, L. Tsetseris, I. McCulloch and T. D. Anthopoulos, *Advanced Functional Materials*, 2019, **29**, 1905810.
- 104 J. Chaopaknam, C. Wechwithayakhlung, H. Nakajima, T. Lertvanithphol, M. Horprathum, T. Sudyoasuk, V. Promarak, A. Saeki and P. Pattanasattayavong, *Applied Physics Letters*, 2021, **119**, 063301.
- 105 W. J. Biermann and R. H. McCorkell, *Canadian Journal of Chemistry*, 1967, **45**, 2846–2849.
- 106 M. R. Buchner and M. Müller, *Dalton Transactions*, 2021, **50**, 7246–7255.
- 107 M. Joos, M. Conrad, R. Merkle, T. Schleid, J. Maier, R. E. Dinnebier and S. Bette, *Dalton Transactions*, 2021, **50**, 6949–6961.
- 108 N. P. Crawford and G. A. Melson, *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1969, **0**, 1049–1052.
- 109 Jiro Matsuura, Yasuhiro Karakawa and Toru Murakami, *Bunseiki Kagaku*, 1965, **14**, 267–269.
- 110 D. R. Cousins and F. A. Hart, *Journal of Inorganic and Nuclear Chemistry*, 1968, **30**, 3009–3015.
- 111 J. L. Martin, L. C. Thompson, L. J. Radonovich and M. D. Glick, *Journal of the American Chemical Society*, 1968, **90**, 4493–4494.
- 112 H. Böhland and H. Steinecke, *Zeitschrift für anorganische und allgemeine Chemie*, 1981, **148**, 136–148.
- 113 H. Bialowons, M. Müller and B. G. Müller, *Zeitschrift für anorganische und allgemeine Chemie*, 1995, **621**, 1227–1231.
- 114 A. Dawson, A. Parkin, S. Parsons, C. R. Pulham and A. L. C. Young, *Acta Crystallographica*, 2002, **E58**, i95–i97.
- 115 P. Brand and J. Schmidt, *Zeitschrift für anorganische und allgemeine Chemie*, 1966, **348**, 257–260.
- 116 S. Troyanov, *Russian Journal of Inorganic Chemistry*, 1993, **38**, 208–211.
- 117 A. M. Golub and T. Lishko, *Russian Journal of Inorganic Chemistry*, 1970, **15**, 783.
- 118 J. A. Sommers, L. Palys, N. P. Martin, D. B. Fast, M. Amiri and M. Nyman, *Journal of the American Chemical Society*, 2022, **144**, 2816–2824.
- 119 H. Böhland and P. Malitzke, *Zeitschrift für Naturforschung B*, 1965, **20**, 1126–1127.
- 120 E. Shurdha, C. E. Moore, A. L. Rheingold, S. H. Lapidus, P. W. Stephens, A. M. Arif and J. S. Miller, *Inorganic Chemistry*, 2013, **52**, 10583–10594.
- 121 S. Triki, F. Bérézovsky, J. Sala Pala and M.-T. Garland, *Inorganica Chimica Acta*, 2000, **308**, 31–36.
- 122 H. Böhland and E. Zenker, *Journal of the Less Common Metals*, 1968, **14**, 397–402.

- 123 L. F. Larkworthy, A. J. Roberts, B. J. Tucker and A. Yavari, *Journal of the Chemical Society, Dalton Transactions*, 1980, 262–268.
- 124 H. Funk and H. Böhland, *Zeitschrift für anorganische und allgemeine Chemie*, 1963, **169**, 168–172.
- 125 H. Funk and H. Böhland, *Zeitschrift für Chemie*, 1961, **1**, 190–190.
- 126 M. Sarker, *Transition Metal Chemistry*, 1992, **17**, 514–516.
- 127 H. Böhland and E. Nieman, *Zeitschrift für anorganische und allgemeine Chemie*, 1965, **164**, 225–233.
- 128 C. J. Horn and T. M. Brown, *Inorganic Chemistry*, 1972, **11**, 1970–1972.
- 129 J. R. Knox and K. Eriks, *Inorganic Chemistry*, 1968, **7**, 84–90.
- 130 A. Bino, F. A. Cotton and P. E. Fanwick, *Inorganic Chemistry*, 1979, **18**, 3558–3562.
- 131 C. Boukouvala, D. Kaltsas and L. Tsetseris, *Journal of Physics: Condensed Matter*, 2017, **29**, 485703.
- 132 H. G. von Schnering, W. May and K. Peters, *Zeitschrift für Kristallographie - Crystalline Materials*, 1993, **208**, 368–369.
- 133 H. Sano and M. Akane, *Chemistry Letters*, 1973, **2**, 43–46.
- 134 H. S. Trop, A. Davison, A. G. Jones, M. A. Davis, D. J. Szalda and S. J. Lippard, *Inorganic Chemistry*, 1980, **19**, 1105–1110.
- 135 F. A. Cotton, A. Davison, W. H. Ilsey and Harvey S. Trop, *Inorganic Chemistry*, 1979, **18**, 2719–2723.
- 136 L. C. Hurd and B. J. Babler, *Industrial & Engineering Chemistry Analytical Edition*, 1936, **8**, 112–114.
- 137 W. Geilmann, F. W. Wrigge and F. Weibke, *Zeitschrift für anorganische und allgemeine Chemie*, 1932, **208**, 217–224.
- 138 G. Winkhaus and P. Ziegler, *Zeitschrift für anorganische und allgemeine Chemie*, 1967, **350**, 51–61.
- 139 S. J. Patel, *Boletin de la Sociedad Chilena de Quimica*, 1972, **19**, 13–14.
- 140 S. J. Patel, *Boletin de la Sociedad Chilena de Quimica*, 1972, **19**, 15–16.
- 141 O. Stähler and W. Preetz, *Zeitschrift für anorganische und allgemeine Chemie*, 2000, **626**, 2077–2080.
- 142 J.-U. Rohde and W. Preetz, *Zeitschrift für anorganische und allgemeine Chemie*, 1998, **624**, 1319–1323.
- 143 K. Bütje and W. Preetz, *Zeitschrift für Naturforschung B*, 1987, **43**, 371–381.
- 144 Yu. N. Kukushkin, L. V. Vrublevskaia, S. I. Bakhireva and E. N. Kalyukova, *Russian Journal of Inorganic Chemistry*, 1980, **25**, 723–726.
- 145 H. S. Sangari, G. S. Sodhi and J. Kaur, *Thermochimica Acta*, 1990, **171**, 49–55.
- 146 W. L. G. Gent and C. S. Gibson, *Journal of the Chemical Society (Resumed)*, 1949, 1835–1840.
- 147 P. L. Goggin, I. J. McColm and R. Shore, *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1966, 1314.
- 148 S. J. Patel, D. B. Sowerby and D. G. Tuck, *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1967, 1187–1190.
- 149 S. J. Patel and D. G. Tuck, *Canadian Journal of Chemistry*, 1969, **47**, 229–233.
- 150 S. J. Patel, *Journal of Inorganic and Nuclear Chemistry*, 1971, **33**, 17–22.
- 151 I. K. Taimni, *Journal of the Chemical Society (Resumed)*, 1931, 2433–2435.
- 152 E. Söderbäck, *Justus Liebigs Annalen der Chemie*, 1919, **419**, 217–322.
- 153 G. Thiele and D. Messer, *Zeitschrift für anorganische und allgemeine Chemie*, 1976, **421**, 24–36.
- 154 J. Y. Lee, S. Ling, S. P. Argent, M. S. Senn, L. Cañadillas-Delgado and M. J. Cliffe, *Chemical Science*, 2021, **12**, 3516–3525.
- 155 M. J. Cliffe, E. N. Keyzer, A. D. Bond, M. A. Astle and C. P. Grey, *Chemical Science*, 2020, **11**, 4430–4438.
- 156 K.-P. Xie, W.-J. Xu, C.-T. He, B. Huang, Z.-Y. Du, Y.-J. Su, W.-X. Zhang and X.-M. Chen, *CrystEngComm*, 2016, **18**, 4495–4498.
- 157 D.-X. Liu, K.-P. Xie, W.-X. Zhang, M.-H. Zeng and X.-M. Chen, *CrystEngComm*, 2021, **23**, 2208–2214.
- 158 H. A. Evans, Y. Wu, R. Seshadri and A. K. Cheetham, *Nature Reviews Materials*, 2020, **5**, 196–213.
- 159 S. B. Hendricks and H. E. Merwin, *American Journal of Science*, 1928, **15**, 487–494.
- 160 R. A. Bailey and T. W. Michelsen, *Journal of Inorganic and Nuclear Chemistry*, 1972, **34**, 2671–2673.
- 161 C. Mahr, *Zeitschrift für anorganische und allgemeine Chemie*, 1932, 313–316.
- 162 C. J. Howard, B. J. Kennedy and P. M. Woodward, *Acta Crystallographica*, 2003, **B59**, 463–471.
- 163 A. M. Glazer, *Acta Crystallographica*, 1972, **B28**, 3384–3392.
- 164 J. A. Hill, A. L. Thompson and A. L. Goodwin, *Journal of the American Chemical Society*, 2016, **138**, 5886–5896.
- 165 H. L. B. Boström, J. A. Hill and A. L. Goodwin, *Physical Chemistry Chemical Physics*, 2016, **18**, 31881–31894.
- 166 H. L. B. Boström, *CrystEngComm*, 2020, **22**, 961–968.
- 167 V. J. Minkiewicz, D. E. Cox and G. Shirane, *Solid State Communications*, 1970, **8**, 1001–1005.
- 168 M. Bukowska-Strzyzewska, A. Cygański, W. Maniukiewicz, A. Turek and K. Zagajewska, *Journal of Chemical Crystallography*, 1994, **24**, 425–429.
- 169 Y. Kuniyasu, Y. Suzuki, M. Taniguchi and A. Ouchi, *Bulletin of the Chemical Society of Japan*, 1987, **60**, 179–183.
- 170 C. S. Yeh, *Microchemical Journal*, 1969, **14**, 279–288.
- 171 D. Xu, W.-T. Yu, X.-Q. Wang, D.-R. Yuan, M.-K. Lu, P. Yang, S.-Y. Guo, F.-Q. Meng and M.-H. Jiang, *Acta Crystallographica*, 1999, **C55**, 1203–1205.
- 172 Y. Yunxing, Q. Fang, D. Yuan, Y. Tian, M. Jiang, I. D. Williams and C. Zhigang, *Acta Chimica Sinica*, 1999, **57**, 1257–1261.
- 173 M. Iizuka and T. Sudo, *Zeitschrift für Kristallographie*, 1968, **126**, 376–378.
- 174 Y.-P. Tian, W.-T. Yu, Q. Fang, X.-Q. Wang, D.-R. Yuan, D. Xu and M.-H. Jiang, *Acta Crystallographica*, 1999, **C55**, 1393–1395.

- 175 X. Q. Wang, D. Xu, D. R. Yuan, Y. P. Tian, W. T. Yu, S. Y. Sun, Z. H. Yang, Q. Fang, M. K. Lu, Y. X. Yan, F. Q. Meng, S. Y. Guo, G. H. Zhang and M. H. Jiang, *Materials Research Bulletin*, 1999, **34**, 2003–2011.
- 176 A. A. Khandar, A. Klein, A. Bakhtiari, A. R. Mahjoub and R. W. H. Pohl, *Journal of Solid State Chemistry*, 2011, **184**, 379–386.
- 177 M. Porai-Koshits, *Zhurnal Strukturnoi Khimii*, 1963, **4**, 584.
- 178 M. Weil and T. Häusler, *Acta Crystallographica*, 2014, **E70**, 48–50.
- 179 M. Iizumi, *Annual Report of Bunkyo University*, 1978, **March**, 65–68.
- 180 G.-H. Li, Q. Fang, G. Xue and W.-T. Yu, *Chinese Journal of Inorganic Chemistry*, 2005, **21**, 91–94.
- 181 V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Crystal Growth & Design*, 2014, **14**, 3576–3586.
- 182 P. G. Jones and E. Bembenek, *Acta Crystallographica*, 1992, **C48**, 1361–1362.
- 183 S.-F. Lu, M.-Y. He and J.-L. Huang, *Chinese Journal of Structural Chemistry*, 1982, **1**, 72–76.
- 184 Z. Gałdecki, M. L. Główska and B. Goliński, *Acta Crystallographica*, 1976, **B32**, 2319–2321.
- 185 T. Cherkasova, *Russian Journal of Inorganic Chemistry*, 1992, **37**, 71–73.
- 186 A. Cyganski, *Roczniki Chemii*, 1967, **41**, 39–44.
- 187 A. Cyganski, *Roczniki Chemii*, 1965, **39**, 193–199.
- 188 A. Cyganski, *Roczniki Chemii*, 1964, **38**, 1699.
- 189 A. Cyganski, *Roczniki Chemii*, 1963, **37**, 1543–1545.
- 190 A. Turek and A. Cyganski, *Thermochimica Acta*, 1994, **232**, 205–214.
- 191 P. P. Singh and S. B. Sharma, *Journal of the Indian Chemical Society*, 1975, **52**, 617–622.
- 192 M. Fleck, *Acta Crystallographica*, 2004, **C60**, i63–i65.
- 193 A. R. Oganov and S. Ono, *Nature*, 2004, **430**, 445–448.
- 194 M. Murakami, K. Hirose, K. Kawamura, N. Sata and Y. Ohishi, *Science*, 2004, **304**, 855–858.
- 195 F. Rodi and D. Babel, *Zeitschrift für anorganische und allgemeine Chemie*, 1965, **336**, 17–23.
- 196 C. D. Martin, W. A. Crichton, H. Liu, V. Prakapenka, J. Chen and J. B. Parise, *American Mineralogist*, 2006, **91**, 1703–1706.
- 197 Y. Shirako, Y. G. Shi, A. Aimi, D. Mori, H. Kojitani, K. Yamaura, Y. Inaguma and M. Akaogi, *Journal of Solid State Chemistry*, 2012, **191**, 167–174.
- 198 D. P. Dobson, S. A. Hunt, A. Lindsay-Scott and I. G. Wood, *Physics of the Earth and Planetary Interiors*, 2011, **189**, 171–175.
- 199 A. Lindsay-Scott, D. Dobson, F. Nestola, M. Alvaro, N. Casati, C. Liebske, K. S. Knight, R. I. Smith and I. G. Wood, *Journal of Applied Crystallography*, 2014, **47**, 1939–1947.
- 200 F. L. Bernal, K. V. Yusenko, J. Sottmann, C. Drathen, J. Guignard, O. M. Løvvik, W. A. Crichton and S. Margadonna, *Inorganic Chemistry*, 2014, **53**, 12205–12214.
- 201 E. T. Keve, S. C. Abrahams and J. L. Bernstein, *The Journal of Chemical Physics*, 2003, **51**, 4928–4936.
- 202 H. Krautscheid and S. Gerber, *Acta Crystallographica*, 2001, **C57**, 781–783.
- 203 J. Valkonen and M. Günes, *Acta Crystallographica*, 2001, **E57**, i52–i54.
- 204 G. Thiele and W. Kehr, *Zeitschrift für anorganische und allgemeine Chemie*, 1984, **515**, 199–206.
- 205 N. L. Coker, J. A. Krause Bauer and R. C. Elder, *Journal of the American Chemical Society*, 2004, **126**, 12–13.
- 206 J. Bandemehr, M. Conrad and F. Kraus, *Acta Crystallographica*, 2017, **E73**, 1073–1075.
- 207 A. Mawby and G. E. Pringle, *Journal of Inorganic and Nuclear Chemistry*, 1972, **34**, 2213–2217.
- 208 C. Wickleder and P. Larsen, *Zeitschrift für anorganische und allgemeine Chemie*, 2001, **627**, 1279–1282.
- 209 G. Bombieri, P. T. Moseley and D. Brown, *Journal of the Chemical Society, Dalton Transactions*, 1975, 1520–1523.
- 210 O. Reckeweg and F. J. DiSalvo, *Zeitschrift für Naturforschung B*, 2016, **71**, 161–164.
- 211 N. M. Byrne, M. H. Schofield, A. D. Nicholas and C. L. Cahill, *Dalton Transactions*, 2021, **50**, 9158–9172.
- 212 R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coordination Chemistry Reviews*, 1971, **6**, 407–445.
- 213 C. D. Delfs, B. N. Figgis, E. S. Kucharski and P. A. Reynolds, *Journal of the Chemical Society, Dalton Transactions*, 1989, 1779–1785.
- 214 Z. V. Zvonkova, *Zhurnal Fizicheskoi Khimii*, 1953, **27**, 100.
- 215 S. Biswas, S. Ma, S. Nuzzo, B. Twamley, A. T. Russell, J. A. Platts, F. Hartl and R. J. Baker, *Inorganic Chemistry*, 2017, **56**, 14426–14437.
- 216 A. Merchant, S. Batzner, S. S. Schoenholz, M. Aykol, G. Cheon and E. D. Cubuk, *Nature*, 2023, 1–6.
- 217 J. Schmidt, H.-C. Wang, T. F. T. Cerqueira, S. Botti and M. A. L. Marques, *Scientific Data*, 2022, **9**, 64.
- 218 R. E. A. Goodall, A. S. Parackal, F. A. Faber, R. Armiento and A. A. Lee, *Science Advances*, 2022, **8**, eabn4117.
- 219 A. K. Cheetham, R. Seshadri and F. Wudl, *Nature Synthesis*, 2022, **1**, 514–520.
- 220 N. Mounet, M. Gibertini, P. Schwaller, D. Campi, A. Merkys, A. Marrazzo, T. Sohier, I. E. Castelli, A. Cepellotti, G. Pizzi and N. Marzari, *Nature Nanotechnology*, 2018, **13**, 246–252.
- 221 Y. Song, E. M. D. Siriwardane, Y. Zhao and J. Hu, *ACS Applied Materials & Interfaces*, 2021, **13**, 53303–53313.
- 222 D. Campi, N. Mounet, M. Gibertini, G. Pizzi and N. Marzari, *ACS Nano*, 2023, **17**, 11268–11278.