

Topological Motifs in Cyanometallates: From Building Units to Three-Periodic Frameworks

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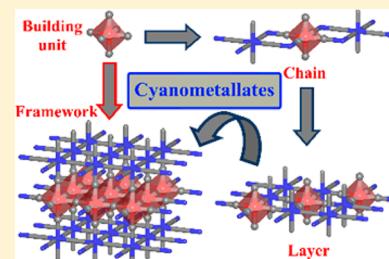
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Supporting Information

ABSTRACT: This review focuses on topological features of three-periodic (framework) *p*, *d*, and *f* metal cyano complexes or cyanometallates, i.e. coordination compounds, where CN⁻ ligands play the main structure-forming role. In addition, molecular, one-periodic (chain), and two-periodic (layer) cyanometallates are considered as possible building blocks of the three-periodic cyanometallates. All cyanometallates are treated as systems of nodes (mononuclear, polynuclear, or transitional metal cluster complexes) joined together via CN-containing spacers. The most typical nodes and spacers as well as methods of their connection are described and systematized. Particular attention is paid to the overall structural motifs in the three-periodic cyanometallates, especially to the relations between the local coordination (coordination figure) of structural units and the entire framework topology. The chemical factors are discussed that influence the cyanometallate topological properties due to modification of nodes, spacers, or coordination figures.



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1. INTRODUCTION

Transition metal or lanthanide coordination compounds, where CN⁻ ligands play the main structure-forming role, so-called *cyano complexes* or *cyanometallates*, have been the subject of sustainable interest for the last several years (Figure 1),^{1–5} due to their valuable magnetic properties,^{6–14} including ferromagnetism at room temperature^{15–17} and spin-crossover.^{18–21} Some crystals of cyano complexes are known to possess nonlinear optic properties.²² Our review concerns mainly 3D framework cyanometallates, which have a great structural diversity as well as valuable physical properties. Cyano groups in such cyanometallates can provide an ordered arrangement of mono- and/or polyatomic magnetic centers as well as magnetic

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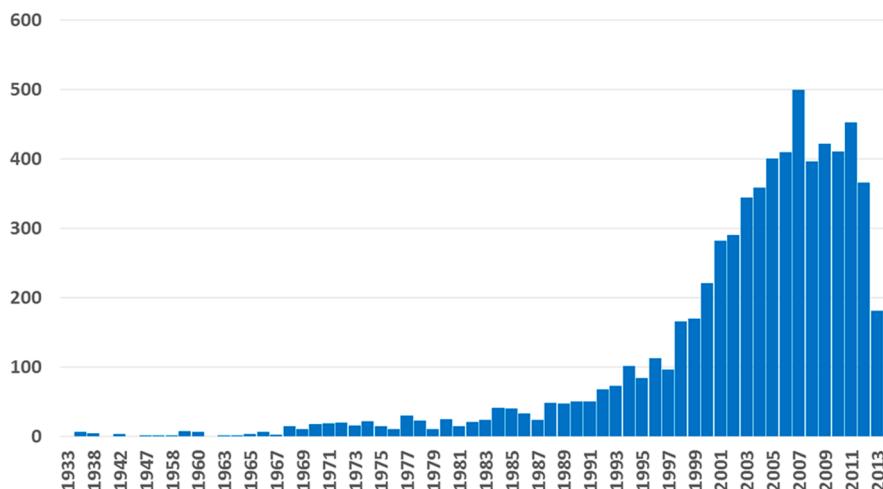


Figure 1. Distribution of the structures of cyano complexes deposited in the CSD and the ICSD on the year of publication up to 2013.

coupling.¹ Some cyanometallate frameworks were found to switch reversibly their magnetization under electrochemical^{23–25} or light stimulation^{26–29} due to redox processes or spin-crossover of the 3d metal cations. Accordingly, these compounds are important for magnetic materials design.^{15,16,30,31} Moreover, similar to coordination networks, some of the framework cyanometallates were discovered to form inclusion compounds⁵ that enabled their usage as cyanometallate-based molecular sieves³² for reversible sorption of carbon dioxide and hydrogen.^{33–36}

The synthetic methods and physicochemical properties of cyanometallates were discussed in a number of reviews^{1–5,13} also in relation to coordination of complexing atoms and ligands.^{12,37} In the last 10–15 years, special attention has been drawn to the cyanometallate topology, i.e. to the methods of connecting these primary building units into the polymeric motifs that are crucial for the design of coordination compounds.^{38–51}

The first attempts to explore the topological relations between different cyanometallate frameworks originated from the 1930s,^{52,53} and the description was based on the notion of structure type. The most widespread cyanometallate structural types were characterized as Prussian Blue analogues^{54–57} (*aka* “cubic frameworks”),^{58–61} diamondoid networks^{62–66} (*aka* cristobalite-like lattices),^{67,68} and PtS-type structures.^{69–72} The conventional names of topological types⁷³ appeared in the cyanometallate literature only in the 2000s,^{74–76} and now they have become more and more popular. However, only in ~12% of original publications the authors do analyze the overall topological properties of cyanometallate frameworks. To the best of our knowledge, there are no examples of topological taxonomy of the frameworks or detailed analysis of relations between different levels of the structure organization of cyanometallates.

This work is intended to fill this gap and, in contrast to all previous reviews of cyano complexes, focuses on topological features of three-periodic (framework) *p*, *d*, and *f* metal cyano complexes containing organic and inorganic ligands. In addition, molecular, one-periodic (chain) and two-periodic (layer) cyanometallates will also be outlined in their relation to the three-periodic cyanometallate topological motifs. This is necessary for two reasons: (i) to show the role of particular building blocks in cyanometallates of different periodicity (see Section 4.2); (ii) to explore how the low-periodic cyanome-

tallate groups can serve as building units in the framework cyanometallates (see Section 5.3).

2. DEFINITION OF CYANOMETALLATES

Cyanometallates are considered in this review (i) as crystalline substances, where the long-range order, *periodicity*, is the determinant factor, and (ii) as coordination compounds, where the main attention is paid to the interactions “metal–ligand”. In this section, we briefly characterize these two points of view.

2.1. *n*-Periodic cyanometallates

We call *n*-periodic cyanometallates the polymeric complexes, where bridging cyano groups provide the *n*-periodic architecture of the network of metal atoms, polynuclear complex groups, or clusters (hereinafter we call them *cyano-bridged*). The other ligands (if any) are either supposed to be terminal or included only in finite (molecular) polynuclear complex groups. In other words, removal of all other ligands does not cause a disjunction of the polymeric complex into separated parts. The complexes where cyano groups do not play such a key structure-forming role we call *cyano-containing*. We prefer the term “*n*-periodic” rather than “*n*-dimensional” (0D, 1D, 2D, or 3D) because the last one does not imply that the group is infinite; it just indicates the dimensionality of the space, where the group can be embedded. For example, a 3D object can be 0-periodic (a finite cluster), 1-periodic (a tube), 2-periodic (a double layer), or 3-periodic. We also distinguish the coordination compounds, which contain cyano ligands, from *n*-periodic cyanometallates, although all of them comprise a *cyanometallate motif*, i.e. the fragments of the complex that are *cyano-bridged*. We will systematically show that the same cyanometallate motif can build coordination polymers of different periodicity (see Section 5.3).

Structural information was mainly taken from the Cambridge Structural Database (CSD, release 5.35) and the Inorganic Crystal Structure Database (ICSD, release 2014/1). Totally, we found 3877, 940, 681, and 918 zero-, one, two-, and three-periodic cyano-containing complexes, respectively, as well as 197 compounds with mixed zero-, one, two-, or three-periodic structural motifs, and 12 cyano salts of alkali or alkaline-earth metals that cannot be considered as coordination compounds and therefore are not analyzed in detail. These 6625 structures included isostructural series and chemically identical frameworks that differ only by the extra-framework cations; we have

Table 1. Distributions of the Cyano-Containing Complexes on Periodicity and Ligand Terminal (t) or Bridging (μ) Coordination Modes

Ligand type and coordination mode	Periodicity of structure groups									Total
	0	1	2	3	1 + 0	2 + 0	3 + 0	2 + 1	3 + 1	
$t\text{-CN}$	547	-	-	-	-	-	-	-	-	547
$t\text{-CN}, t\text{-L}$	1472	-	-	-	-	-	-	-	-	1472
Only terminal (t) ligands	2019	-	-	-	-	-	-	-	-	2019
$\mu\text{-CN}$	-	12	33	214	-	-	-	-	-	259
$\mu\text{-CN}, \mu\text{-L}$	21	17	92	227	-	1	-	12	3	373
Only bridging (μ) ligands	21	29	125	441	-	1	-	12	3	632
$\mu\text{-CN}, t\text{-CN}$	3	7	11	1	-	1	-	-	-	23
$\mu\text{-CN}, t\text{-L}$	430	233	195	228	-	10	14	-	-	1110
$\mu\text{-CN}, t\text{-CN}, t\text{-L}$	789	513	204	70	71	29	4	1	-	1678
$\mu\text{-CN}, \mu\text{-L}, t\text{-CN}$	12	24	19	12	3	1	1	-	-	72
$\mu\text{-CN}, \mu\text{-L}, t\text{-L}$	88	27	35	81	-	3	8	-	-	242
$\mu\text{-CN}, \mu\text{-L}, t\text{-CN}, t\text{-L}$	136	88	84	83	12	9	2	-	-	416
$\mu\text{-L}, t\text{-CN}$	194	15	7	-	3	1	-	-	-	220
$\mu\text{-L}, t\text{-CN}, t\text{-L}$	185	5	-	2	8	-	-	-	-	200
Terminal and bridging ligands	1837	911	556	477	97	54	29	1	-	3962
Total	3877	941	680	918	97	55	29	13	3	6613
Ionic cyanides $M_x(\text{CN})_z$	8									12
Ionic mixed cyanides $M_xL_y(\text{CN})_z$	4									

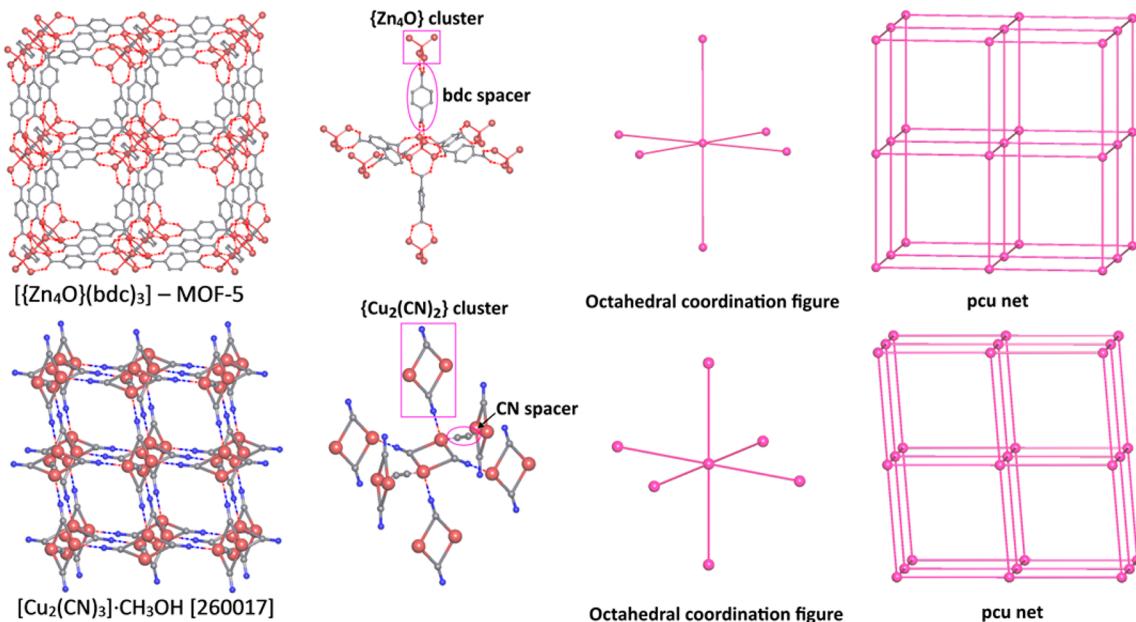


Figure 2. (Top) Fragments of coordination polymeric groups and their topological representations for $[Zn_4O(bdc)_3]$ ($bdc = 1,4\text{-benzenedicarboxylate}$; full list of abbreviations can be found in the Supporting Information), and (bottom) $[Cu_2(CN)_3] \cdot CH_3OH$ [260017]. The intercluster bonds are shown by dashed lines.

considered alkaline-earth metals (Ca, Sr, Ba) and alkali metals except lithium as extra-framework. Among them, there were 748 inorganic (containing no C–C bonds) cyano-containing complexes retrieved from the ICSD as well as 15 crystal structures reported elsewhere. The periodicity of the complexes versus the coordination mode of the cyano group and other ligands is given in Table 1. A detailed analysis will be provided only for the 557 frameworks selected from the 937 (918 3D and 29 3D+0D) three-periodic cyano-containing complexes in the following way:

(i) we have extracted 746 cyanometallates, i.e. the complexes, where the polymeric motifs are formed by only cyano ligands,

while all other ligands can be assigned to the coordination nodes (see Section 2);

(ii) among the 746 complexes, we have selected 557 chemically and/or topologically different frameworks; the other 189 structures differed from them only by extra-framework species (counter-cations, clathrate and solvate molecules).

Additionally we analyzed the role of low-periodic ($n < 3$) cyanometallate groups in the structure of the *heteroleptic* coordination polymers (containing both cyano and other kinds of ligands) compared to *homoleptic* cyanometallates (containing only cyano ligands).

2.2. Cyanometallates as coordination polymers

Since Alfred Werner's time, coordination chemistry has operated with the terms *central atom* (coordination center, M) and *ligands* (L) coordinated to it.⁷⁷ The ligands connected to more than one metal center are *bridging*, and *coordination polymers*,⁷⁸ being a subclass of coordination compounds, can be treated as aggregates of structural fragments (*nodes*) connected via bridging ligands called *spacers* or *linkers*.^{79–87} The “node and spacer” concept^{81–87} reputedly played a seminal role in the chemistry of coordination polymers. The structural fragment can consist of a single metal atom, a metal atom together with coordinated terminal ligands (ML_x), or a polynuclear complex $\{M_n(t\text{-}L)_x(\mu\text{-}L)\}_y$. From traditional coordination chemistry's point of view, the bridging ligands $\mu\text{-}L$ are to be treated as spacers. However, their role in the structure of a coordination polymer is quite different. The spacers connect the nodes into an extended structure, while the $\mu\text{-}L$ ligands merely expand the nodes of the polymer.

A typical example is the coordination polymer $[\text{Zn}_4(\mu_4\text{-O})L_3]$, aka MOF-5, where L is a bridging 1,4-benzenedicarboxylate anion.⁴³ In terms of coordination chemistry, there are two sorts of bridging ligands, a μ_4 -oxo anion centering the Zn_4 tetrahedra and edge-bridged carboxylates (L) linking these tetrahedra into an extended network. According to the “node and spacer” concept, the L ligands become spacers, while the oxo ligands should be included into the $\{\text{Zn}_4\text{O}\}$ nodes, because they do not influence the connectivity of the polymer (Figure 2). Such an interpretation sounds not only topological, but also chemical, since such nodes occur in the series of compounds which differ only by L . Indeed, the difference between the spacer and the bridging ligand is a matter of opinion but often has a chemical reason; in particular, a metal complex can be a spacer (see Section 4.2.1). Similarly, a cyano group can either play the role of spacer or belong to a node. For example, in $[\text{Cu}_2(\text{CN})_3]\cdot\text{CH}_3\text{OH}$ [260017]⁸⁸, each copper atom coordinates four cyano groups, out of which two belong to the $\{\text{Cu}_2(\text{CN})_2\}$ species (Figure 2). Hereafter the CSD or ICSD codes of referred compounds are presented in brackets.

To analyze and classify cyanometallate frameworks, we should explore the method of linking nodes and spacers into a polymeric structure using an appropriate topological approach (see Section 3). In general, the relation “coordination number–coordination polyhedron–topology of coordination polymer” should be established that is of key importance for *crystal engineering*.^{89–91} The underlying practical goal is to obtain routinely a desired 3D arrangement of structural fragments in the crystal by operating with definite, rationally chosen building blocks that often are directly brought into the reaction.^{41–51}

3. TOPOLOGICAL DESCRIPTION OF COORDINATION POLYMERS

3.1. General notions

Topology is a key notion for the structural connectivity of chemical compounds, although chemists often use it without any clear definition.⁹² Sometimes this causes ambiguity. What is meant by the same or different “topology of complex group”, “topology of connecting ligands”, or “topological properties of crystal structure”? In this section, we discuss a modern topological approach that was recently developed first of all for coordination polymers. It is based on a rigorous mathematical definition of topology, which in the case of an atomic group can be formulated as “the totality of the

interatomic bonds under consideration in a crystal”. Such kind of topology is naturally represented in chemistry as a graph, whose vertices and edges correspond to atoms or atomic groups and contacts between them. Any finite, even polynuclear, coordination group is described by a finite (0-periodic) graph, while chain, layer, or framework coordination polymers are represented by 1-, 2-, or 3-periodic (infinite) graphs; such graphs are called *nets*. The topology of a net can be unambiguously described by a set of *topological invariants* (or *indices*)^{93,94} and denoted with one of the following nomenclatures:

- (i) three-letter RCSR symbols⁷³ and related s-d-G-n symbols;⁹⁴
- (ii) EPINET sqcX notation;⁹⁵
- (iii) TOPOS Ndk-n symbols.^{96,97}

These different symbols are all of use, since none of the nomenclatures covers the whole diversity of the nets that are intrinsic to coordination polymers. For example, a net with the topology of the diamond structure is denoted as dia (RCR) or sqc6 (EPINET), but has no notation in s-d-G-n and Ndk-n nomenclatures. The jbw-3,4-Cmmm symbol of the s-d-G-n nomenclature denotes a 3,4-coordinated net with the maximal symmetry Cmmm, derived from the RCSR jbw net. The 3,3,6T23 symbol of the Ndk-n nomenclature means that a three-periodic (T) net contains three inequivalent nodes with coordination numbers 3, 3, and 6, and this is the 23th topology among those of three-periodic nets with the same coordination numbers of nodes. Here we should mention that the term “node” is used in different, but interrelated, meanings in coordination and topological chemistry. While in coordination chemistry “node” is a complex group, in topological chemistry “node” coincides with the center of a structural group. This means that the “coordination” node shrinks up to the “topological” node, i.e. to a point. Such operation corresponds to a simplification of the structure (see below).

Each symbol corresponds to a *topological type* (or *isoreticular series*),⁴³ i.e. a series of structures of the same topology. The topological type is the basic taxon in the topological systematics of periodic structures.⁹⁶ At present, more than 100,000 reference topological types are stored in the electronic databases RCSR,⁷³ EPINET,⁹⁵ and TOPOS TTD.^{96,98}

An individual net has an infinite number of *embeddings*, i.e. the ways of implementation in a 3D space. The maximum-symmetry embedding is of most interest, since all other embeddings can be regarded as various ways of its distortion.⁹³

When coordination polymers are topologically arranged, it is important to find a general topological motif determining the way of bonding structural groups irrespective of their internal structure. Such a motif corresponds to an *underlying net* that is derived via a particular *simplification* of the initial atomic network so that the nodes of the underlying net coincide with the barycenters of the structural groups, while the edges correspond to the mono- or polyatomic bridges between them. Different underlying nets can describe the same coordination polymer depending on the choice of structural groups. Each underlying net is assigned to one possible representation of the coordination polymer. Here we use two types of representations, the *standard* one, where the structural groups are complexing atoms and ligands, and the *cluster* one, where polynuclear coordination groups are chosen in accordance with rigorous topological criteria.⁹⁶ In terms of the representation concept, the notions of coordination center (node) and spacer

become formalized; standard and cluster representations allow both simple (monatomic) and complex nodes. Cluster representation is useful to find unevident resemblances between cyano complexes with different polynuclear nodes. For example, in $[\text{Cu}(\text{H}_2\text{O})(\text{en})_2][\text{Cu}(\text{CN})_2(\text{SeCN})]$ [AENCSE10],⁹⁹ $[\text{Cu}_2(\text{CN})_2(2,2'\text{-bipym})]\text{NH}_3$ [CAVLOB],¹⁰⁰ $[\text{Cu}_2(\text{CN})_2(5\text{-Me-2,2'-bipym})]$ [MASSUV],¹⁰¹ $[\text{Cu}_2(\text{CN})_2(\text{pbmbiaz})]$ [OHAPAP],¹⁰² and $[\text{Cu}_4(\text{CN})_3(\text{HMtta})_2]\text{OH}$ [WODHED]¹⁰³ (Table S2), the cluster representation is based on binuclear complex groups and leads to a well-known **cds** framework in all cases,⁹⁶ while the standard representation treats metal atoms as mononuclear nodes and results in different underlying nets: **ths** [AENCSE10, CAVLOB, MASSUV],^{99–101} **utp** [OHAPAP],¹⁰² or **sqc9252** [WODHED]¹⁰³ (Figure 3). The resulting **cds**

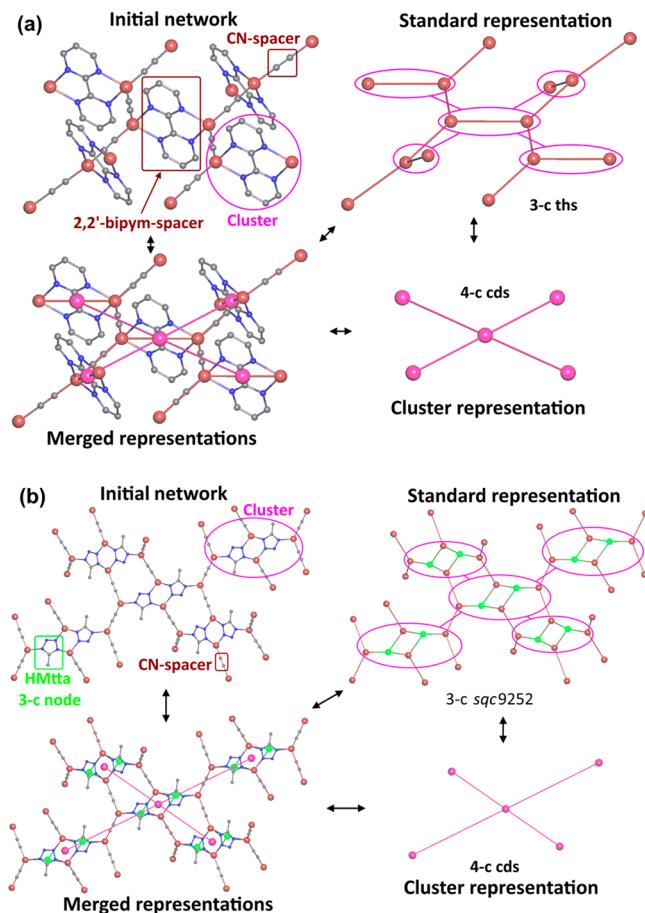


Figure 3. (a) A fragment of the framework $[\text{Cu}_2(\mu\text{-}2,2'\text{-bipym})(\mu\text{-}\text{CN})_2] \cdot n\text{NH}_3$ (hydrogen atoms are omitted for clarity, [CAVLOB]¹⁰⁰) and the corresponding underlying net in the standard (**ths**, in brown) and cluster (**cds**, in magenta) representations; (b) underlying nets in $[\text{Cu}_4(\mu_3\text{-HMtta})_2(\text{CN})_3](\text{OH})$ [WODHED]¹⁰³ in the standard (**sqc9252**, brown and green balls denote Cu atoms and the barycenters of HMtta) and cluster representations (**cds** net is in magenta, nodes correspond to the barycenters of the $[\text{Cu}_4(\text{HMtta})_2]$ complex groups).

underlying nets characterize the same way of connecting structural units despite quite different geometrical parameters and chemical composition of the structures. This makes such an approach quite useful for classification tasks (*cf.* Figure 2).

Thereby, we consider metal atoms, organic and inorganic ligands as well as polynuclear (including cluster) ensembles as components of the framework (they correspond to nodes of the framework underlying net). As was stated above, this concept

generally agrees with the traditional description in coordination chemistry. However, it also allows formalization and analysis of all coordination polymers in the same way.

If the underlying net contains terminal or bridging (one- or two-coordinated) nodes, it can be additionally simplified by removing terminal nodes and replacing spacers with the net edges (Figure 4). The coordination polymers with the same underlying net topology belong to the same topological type.

Using the concept of underlying net, the local topological and geometrical properties of a complex group can also be formalized. All the nodes that are incident to a particular node in the underlying net form a *coordination figure*,^{96,105} which can be considered as an analog of a coordination polyhedron for a node of the underlying net. Since terminal and chelating ligands are ignored in the underlying net, the shape and topology of the coordination figure can differ from those for the complexing atom (Figure 5). If the node corresponds to a ligand, its coordination figure reflects the coordination capabilities of the ligand, but does not indicate *denticity* (i.e., the number of donor atoms of a ligand bonding to the complexing atom, Figure 5) for chelating ligands. Ockwig et al.¹⁰⁵ noticed that the connectivity of an underlying net depends on both the topology and geometry of coordination figures. For example, tetrahedral or octahedral coordination figures mainly result in the topology of a diamond net (**dia**) or a primitive cubic lattice (**pcu**), respectively. The most frequent types of coordination figures and the corresponding most typical 3-periodic underlying nets are shown in Figure 6. Some examples of low-periodic (molecular, chain, or layered) complexes and the corresponding underlying graphs (for molecular compounds) or nets (for polymeric structures) are given in the Supporting Information (Figures S2–S11).

3.2. A method for topological analysis of coordination polymers

The above-described principles of topological analysis and classification of the atomic nets have been implemented into the program package ToposPro,⁹⁸ which we use to describe the coordination figures and to determine the overall topology for the cyano-bridged coordination polymers. The automated algorithm of the analysis of a crystal structure irrespective of its chemical composition and complexity includes the following steps.

(1) Detection of interatomic bonds with the method of intersecting sectors.¹⁰⁶ At this step, the crystal structure connectivity is entirely described with a three-periodic graph that is converted into a finite labeled quotient graph¹⁰⁷ for a subsequent computer analysis. In this study, we take into account only valence bonds, thus ignoring all nonvalence and specific interactions including hydrogen bonds. In proper cases, short metal–metal contacts were also treated as covalent bonds (Section 4.2.2.3).

(2) Simplification of the labeled quotient graph by contracting the atoms of cyano groups (*spacers*; see Section 4.2.1 for details) into their barycenters as well as complex groups into the complexing atoms (for mononuclear complexes) or into the barycenters of polynuclear (cluster) groups (*nodes*; see Section 4.2.2 for details), which gives rise to a primary simplified net in the standard or a cluster representation.^{96,98} The underlying net bearing the information about connection of the structural units is obtained by a subsequent simplification. In 2-periodic and 3-periodic primary simplified nets, the procedure of removing 0- and 1-coordinated

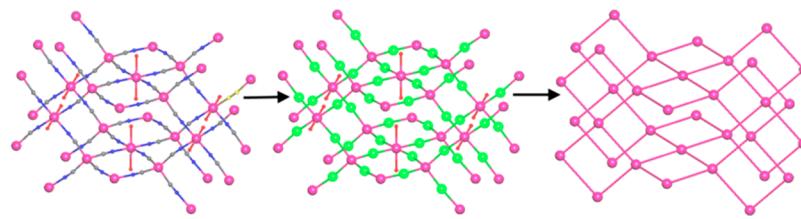


Figure 4. An example of simplification of a coordination polymer $[\text{Cd}_2(\text{H}_2\text{O})_2(\text{CN})_2] \cdot 2(1,4\text{-dioxane})$ [NINHOH]¹⁰⁴ to an underlying pts net. Hydrogen atoms are omitted for clarity; the green balls denote barycenters of the simplified cyano groups.

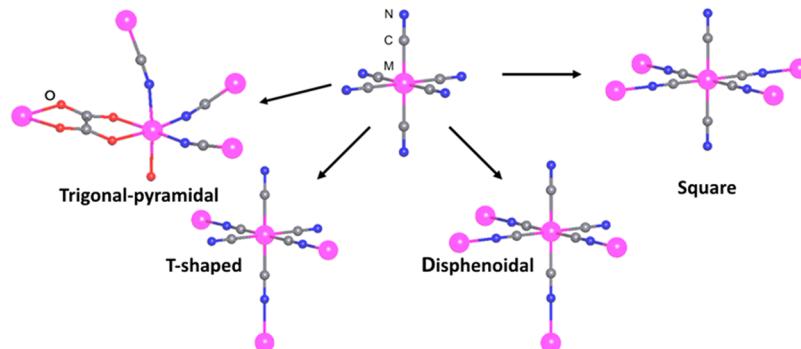


Figure 5. Coordination figures derived from an octacyanometallate building unit by occupation of some coordination sites by terminal or chelate ligands. The coordination figures are formed around the central metal atom by other coordination centers (magenta balls).

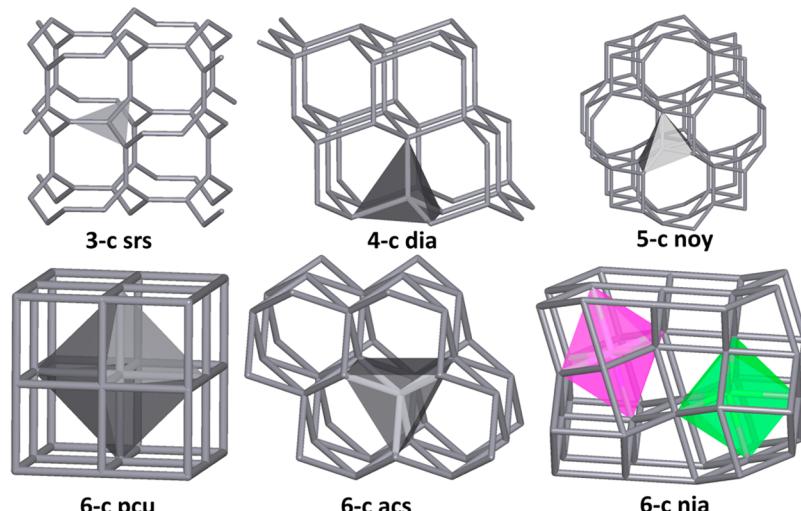


Figure 6. Typical underlying nets with different coordination figures: srs (triangle), dia (tetrahedron), noy (square pyramid), pcu (octahedron), acs (trigonal prism), nia (combination of octahedron and trigonal prism). The coordination figures are highlighted in gray, red, and green.

nodes and replacing 2-coordinated (bridging) nodes by edges is applied (Figures S9–S11), while, in 1-periodic polymers, the 2-coordinated nodes are transformed to edges only if it does not lead to desintegration of the entire net (Figures S5–S8). For finite (0-periodic) complex groups we keep all nodes (ligand centers) including 1-coordinated and 2-coordinated (Figures S2–S4) and, hence, analyze the whole topology of the complex (cf. ref 97).

(3) Separation of the underlying net moieties corresponding to cyanometallate groups. At this step, only bonds between the cyanide ligands and the nodes are considered. If the simplified net does not disintegrate into separate moieties, the compound is classified as a cyanometallate; otherwise, it is considered as a coordination polymer containing cyanometallate groups and the subsequent analysis is performed for each group separately.

(4) Determination of the periodicity $n = 0\text{--}3$ of the underlying net and entanglements (if any) of the nets. Only the coordination polymers with three-periodic underlying nets were taken for the detailed topological analysis, although other cyano complexes were also considered in their relation to the framework cyanometallates.

(5) Calculation of the topological characteristics (indices) of the underlying nets for further classification.

(6) Grouping of the underlying nets into topological types. If the topological indices for all corresponding nodes of the nets under consideration are identical, the nets fall into the same topological type.

(7) Classification of the topological types obtained at the previous step using the TOPOS TTD Collection. The detailed results are given in the Supporting Information.

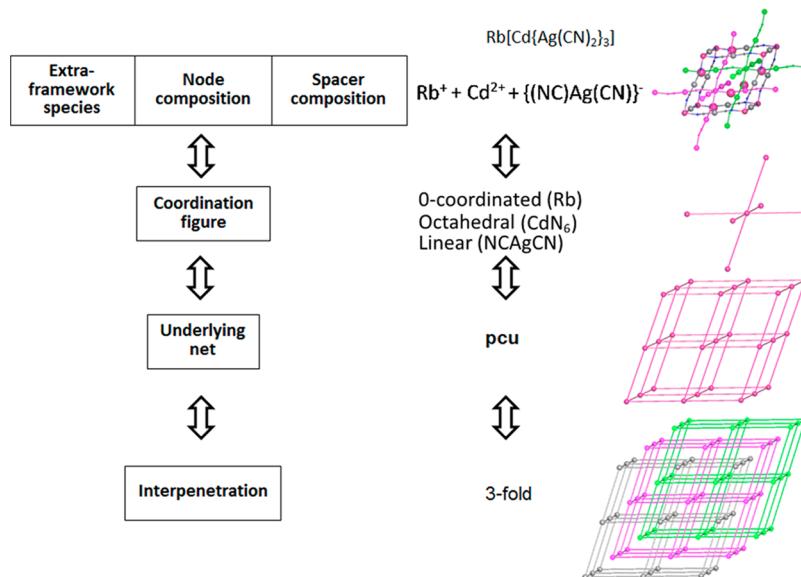


Figure 7. Scheme of hierarchical topological analysis of coordination polymers with an example of Rb[Cd{Ag(CN)₂}₃] [75503].¹⁰⁸ The nodes of the resulting interpenetrating underlying nets coincide with the Cd atoms.

Summarizing, we use the following hierarchical approach for description of cyanometallates (also applicable to any coordination polymer, Figure 7): complexing atoms and ligands form nodes and spacers, which then unite to coordination figures that essentially predetermine the overall topology of the coordination polymer. The subsequent parts of the review will illustrate how this approach works and what correlations “chemical composition–local topology–overall topology” can be found. In section 4, we characterize the most typical finite structural units and the corresponding coordination figures in extended cyanometallates (first two levels in Figure 7), while section 5 is devoted to the relations between the topological properties of both finite and infinite building blocks and the whole cyanometallate motifs (last two levels in Figure 7).

4. BUILDING UNITS OF CYANOMETALLATES

4.1. Complexing atoms and ligands

The chemical composition of the coordination compound intrinsically predetermines the local topological characteristics, such as coordination numbers of complexing atoms or coordination modes of ligands. In turn, the local topology essentially influences the overall structural motif. Thus, to rationalize the correlations between the chemical composition and the architecture of the coordination polymer, first we overview the coordination properties of complexing atoms and ligands.

4.1.1. Complexing atoms. The list of the 22 most frequent complexing atoms in the 6613 cyano-containing complexes is presented in Table 2. The first four elements, Fe, Cu, Ni, and Co, are the most common coordination centers for all coordination compounds, since they are the most frequent in the CSD, but another nine metals (Mn, Pt, Cr, Au, Hg, Gd, Nd, Sm, and Nb) are typical, especially for cyanometallates. At the same time, such metals as Zn, Pd, or Sn are not so abundant for cyanometallates compared to other coordination compounds.

In general, molecular structures are most common for any complexing atom except Cd and Sn (Figure 8). Layered structures are significantly rare compared to chains and

frameworks for Co, Mn, and Pt, while frameworks are most abundant in the Cd complexes.

The distribution of metal atoms on their coordination numbers shows the expected predominance of six- and four-coordinated atoms (Figure 9).

4.1.2. Ligands. The distribution of the 6613 cyano-containing complexes on the ligand composition (Table S4) shows that the five most frequent ligands (along with cyanide ion) are water, 2,2'-bipyridine, carbonyl, chloride, and dimethylformamide. The distribution illustrates the coordination modes of the ligands (Figure 10, Table S4), where the most preferable bridging bidentate mode (B²) occurs for the CN⁻ ion in polymers, and the terminal monodentate mode (M¹) is typical only for chain and molecular complexes, which obviously correlates with the stoichiometric ratio of CN⁻ ion vs coordination centers. Other terminal ligands (water, 2,2'-bipyridine, carbonyl, dimethylformamide, nitrosyl, etc.) are quite diverse in the cyano-containing complexes, while bridging ligands (pyrimidine, pyrazine, 4,4'-bipyridine, sulfide anion, etc.) are not so numerous but are important for tuning the local and overall topology of the cyanometallate motifs (see Section 4.2).

4.2. Spacers, nodes and coordination figures in the layered and framework cyanometallates

Hereafter we dwell on the types of the nodes and spacers as well as on the typical coordination figures found in the three-periodic cyanometallates. In many cases, the building units are similar for cyanometallates irrespective of their periodicity (see also Section 5.3); to demonstrate this, we consider here the 3-periodic complexes along with the 2-periodic ones.

4.2.1. Spacers. 4.2.1.1. CN⁻ ligand as a spacer. Being ambident, the cyano group can donate both carbon and nitrogen atoms for the coordination. Its other feature is to act as a σ-donor or a π-acceptor. According to Sano et al.,¹¹⁰ the orbital levels of the cyano group interacting with the d orbitals of 3d metal cations are arranged in the order $3\sigma \ll 4\sigma < 1\pi < 5\sigma$, so the 5σ orbital makes the largest contribution to the interaction. The ground state of the cyanide ion, $(1\sigma^2)(2\sigma^2)(3\sigma^2)(4\sigma^2)(\pi^4)(5\sigma^2)$, corresponds to a triple bond between the

Table 2. Occurrence of Metal Coordination Centers in the 6613 Cyano-Containing Complexes Deposited in the CSD and ISCD Compared to All Coordination Compounds from the CSD^a

Metal	Coordination numbers in cyano-containing complexes with frequency (%)	Occurrence in cyano-containing complexes (%)	Total occurrence in the CSD (%)
Fe	4 (2.0), 5 (2.6), 6 (80.3) , 7 (4.0), 8 (8.7), 9 (1.5), 10 (0.8)	26.6	5.5
Cu	2 (7.3), 3 (27.6) , 4 (24.3), 5 (28.0), 6 (12.8)	20.7	7.1
Ni	2 (0.3), 3 (0.3), 4 (35.6) , 5 (4.5), 6 (58.7), 7 (0.6)	14.0	3.8
Co	3 (0.3), 4 (2.2), 5 (5.0), 6 (84.8) , 7 (0.7), 8 (6.5), 9 (0.5)	11.3	4.0
Mn	4 (3.5), 5 (4.7), 6 (78.6) , 7 (8.5), 8 (4.2), 9 (0.5)	10.8	2.2
Pt	4 (90.7) , 5 (2.7), 6 (6.4), 10 (0.1)	6.2	2.5
Cr	5 (2.9), 6 (95.2) , 7 (0.6), 8 (0.5), 9 (0.5), 12 (0.3)	5.6	1.3
Mo	4 (7.5), 5 (1.6), 6 (24.5) , 7 (8.9), 8 (38.1), 9 (15.8), 10 (1.6), 11 (1.3), 12 (0.7)	5.5	2.5
Au	2 (79.8) , 3 (2.0), 4 (17.8), 5 (0.1), 6 (0.3)	5.5	1.2
Ru	5 (2.7), 6 (65.3) , 7 (3.9), 8 (24.7), 9 (1.0), 10 (2.5)	5.2	3.4
W	4 (7.0), 5 (0.2), 6 (11.1), 7 (4.3), 8 (65.7), 9 (9.4), 10 (0.5), 11 (0.6), 12 (1.4)	5.1	1.7
Ag	2 (60.4) , 3 (17.4), 4 (18.7), 5 (1.8), 6 (1.7)	5.0	1.9
Re	5 (0.6), 6 (10.2) , 7 (2.0), 8 (1.6), 9 (83.7), 10 (1.9)	4.9	1.4
Cd	4 (36.1) , 5 (8.8), 6 (54.9) , 7 (0.2)	4.8	1.5
Zn	3 (0.6), 4 (37.0) , 5 (20.9), 6 (41.5)	2.5	3.2
Pd	3 (0.5), 4 (91.7) , 5 (4.8), 6 (3.0)	2.1	2.6
Hg	1 (0.9), 2 (33.5) , 3 (7.5), 4 (43.9), 5 (2.2), 6 (7.1), 7 (2.7), 8 (2.2)	1.7	0.7
Gd	7 (4.7), 8 (50.1) , 9 (33.5), 10 (11.7)	1.4	0.3
Nd	7 (0.8), 8 (45.6) , 9 (47.6), 10 (4.9), 11 (1.2)	1.4	0.4
Sm	7 (3.0), 8 (52.4) , 9 (29.9), 10 (0.9), 12 (2.0), 13 (11.8)	1.2	0.4
Sn	3 (4.5), 4 (5.4), 5 (84.6) , 6 (5.5)	1.2	1.7
Nb	7 (10.7), 8 (18.6), 9 (70.7)	1.0	0.3

^aPreferred (with more than 20% occurrence) coordination numbers are showed in bold.

carbon and nitrogen atoms. When the cyano group is C- and N-coordinated to metal centers ($M\text{-CN-}M'$), it acts as a rigid linear spacer. As a result, *d* and *f* cations are associated into either finite (0-periodic) polynuclear groups or infinite (one-, two-, or three-periodic) coordination polymers.

X-ray structural analysis often fails to distinguish the carbon and nitrogen atoms of the cyano group, since they have close atomic scattering factors. Meanwhile, neutron diffraction, which perfectly recognizes the N and C positions, is still not widespread; therefore, analysis of the bond lengths $M\text{-N}$ and $M\text{-C}$ as well as the bond angles $M\text{-N-C}$ and $M\text{-C-N}$ seems to be helpful. Figure 11 represents a distribution of 3465 bond angles $M\text{-N-C}$ and $M\text{-C-N}$ over 1478 *d* metal cyano-containing complexes of any periodicity with ordered crystal

structure and bidentate bridging coordination of the cyano group found in the CSD.¹¹¹ The $M\text{-C-N}$ bond angle is usually almost flat, while the $M\text{-N-C}$ one essentially deviates from 180° .

Rarely, the μ_3 -bridging cyano groups bind two metal ions via the nitrogen atom; for example, this coordination mode was found in three isostructural compounds $\text{Cd}_2[\text{Os}(\text{CN})_6]$, $\text{Cd}_2[\text{Ru}(\text{CN})_6]$, and $\text{Mn}_2[\text{Fe}(\text{CN})_6]$ [417821, 417822, 417824].¹¹² The μ_4 -bridging coordination mode is observed in LiCN [77321].¹¹³ Being simplified, these cyano groups are contracted to three- or four-coordinated nodes of the underlying net (Figure 12).

Besides the cyano group, in the three-periodic cyanometallates, various complex fragments with exactly two cyano groups involved in the network extension can act as spacers. A classical example is a linear dicyanometallate anion, $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Cu, Ag, Au}$). At this point, traditional coordination chemistry regarding a two-coordinated metal ion as a coordination center drifts apart from the topological approach. If such a complex fragment is considered as a two-coordinated node, the resulting net can always be further simplified (see above). The node together with the two bridging cyano groups can be considered as a complex spacer in the framework or as an edge in the underlying net. It should always be kept in mind that, within the topological approach, such a rather long edge is topologically equivalent to a short “cyanide” one, but the resulting structures are geometrically quite different. Hereafter we consider such metal-containing groups as spacers.

4.2.1.2. Linear $[\text{M}(\text{CN})_2]^{n-}$ complexes. In the cyanometallates, Cu^+ , Hg^{2+} , Ag^+ , or Au^+ cations usually form a linear fragment $[\text{M}(\text{CN})_2]^-$ (Figure 13). Analysis of the CSD data gives the averaged distance between the terminal nitrogen atoms as 5.95, 6.36, or 6.22 Å for $\text{M} = \text{Cu, Ag, or Au}$, respectively, which is much larger than the length of the cyano group (~1.2 Å). The mercury-containing spacers are quite rare. In $[\text{Cu}_3(\text{CN})_4(\text{NH}_3)_2\{\text{Hg}(\text{CN})_2\}]$ [172069],¹¹⁴ a neutral fragment $[\text{Hg}(\text{CN})_2]$ with a N···N distance of 6.36 Å plays the role of spacer. Such a prolonged and nonvoluminous spacer predetermines porous cyanometallate frameworks and interpenetrating structures (see below). Note that these spacers were chosen to include trans-plutonium cations into three-periodic cyanometallates.^{115,116} Similar spacers $[\text{Hg}(\text{CN})_2(\text{ONO}_2)]^-$ and $[\text{Ag}(\text{CN})_2(3\text{-C}_5\text{H}_4\text{NI})]^-$ with a *T* shaped coordination of metal and cyano groups in *trans* positions appear in 3-periodic $[\text{Hg}(\text{CN})_2\text{AgNO}_3(\text{H}_2\text{O})_2]$ [31920]¹¹⁷ and 2-periodic $[\text{Ag}_2\text{Fe}(\text{CN})_4(3\text{-C}_5\text{H}_4\text{NI})_3]\cdot(3\text{-C}_5\text{H}_4\text{NI})$ [RIRCAZ01],¹¹⁸ respectively.

4.2.1.3. *d* Metal complexes with two bridging cyano groups $\{M(\text{CN})_2L_n\}$. The transition metal cyano complexes $\{M(\text{CN})_2L_n\}$ (usually $n = 2\text{-}4$) can act as spacers if all L are terminal ligands. Typical examples are *trans*- $\{\text{Cu}(\text{CN})_2(\text{H}_2\text{O})_2\}$ in $\text{Cu}_2[\text{Re}_4\text{Te}_4(\text{CN})_{12}] \cdot 4\text{H}_2\text{O}$ [281122],¹²⁵ *trans*- $\{\text{Cu}(\text{CN})_2(\text{dmf})_4\}$ in $[\text{Cu}_5(\text{dmf})_4(\text{CN})_6]$ [DOLXOR]¹²¹ (Figure 13e), and *trans*- $\{\text{CuPy}_2(\text{CN})_2\}$ in $[\text{Ag}_2\text{Cu}_3\text{Py}_6(\text{CN})]$ [DEH-MEJ].¹²⁶ Terminal ligands L can be chelating, such as ethylenediamine coordinated by Ni^{2+} in $[\text{FeNi}_3(\text{CN})_6(\text{en})_6]\cdot(\text{PF}_6)_2$ [NOBLOF]¹²² (Figure 13f), 3-(aminopropyl)amine (L) coordinated by Cu^{2+} in $[\{\text{CuL}_2\}_3\text{Fe}(\text{CN})_6](\text{ClO}_4)_2$ [MAX-BOC01],¹²⁷ propylenediamine in $[\text{FeNi}_3(\text{CN})_6(1,3\text{-pn})_6]\cdot(\text{PF}_6)_2$ [NOBLUL],¹²² and acetylacetone coordinated by rhenium in $[\text{Mn}(\text{CN})_4\{\text{Re}(\text{acac})_2\}_2]$ [VODYIW],¹²⁸ or macroheterocyclic, such as 18-crown-6 (L) in $[\text{Cd}_5(\text{CN})_{10}L]\cdot 3\text{EtOH}$ [NANPUN].¹²⁹ A spacer with $n = 3$, $[(\text{CN})\{(\text{R})_3\text{Sn}\}(\text{CN})]^-, R$

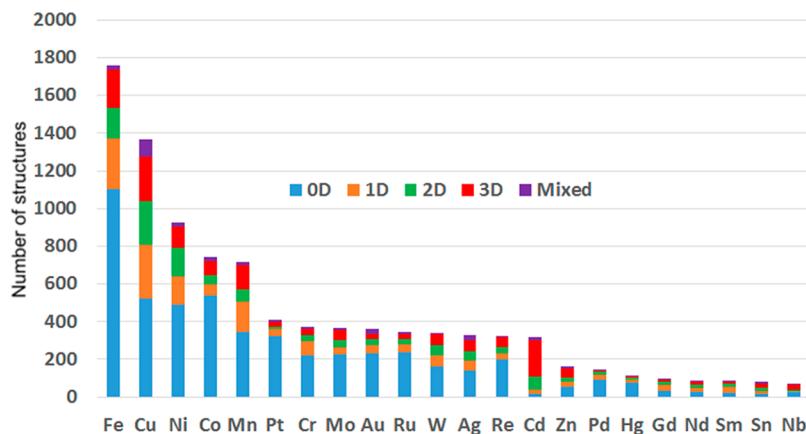


Figure 8. Occurrence of the most abundant complexing atoms in the 6613 cyano-containing complexes with molecular (0D), chain (1D), layer (2D), framework (3D), as well as mixed-periodic (containing motifs of different periodicity) structure.

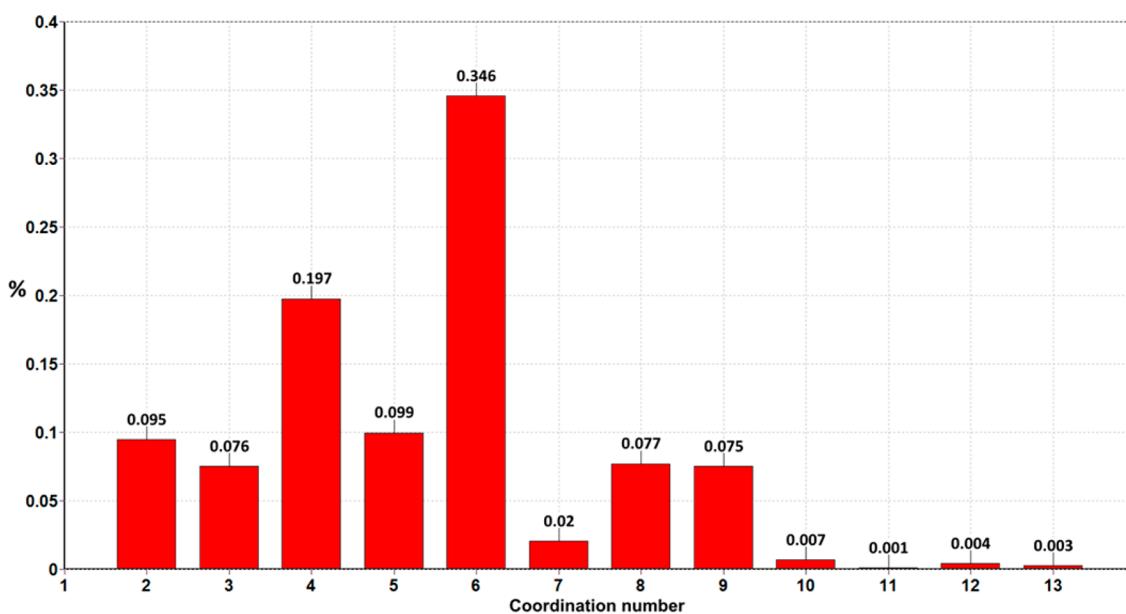


Figure 9. Distribution of coordination numbers of metal atoms in the 6613 cyano-containing complexes.

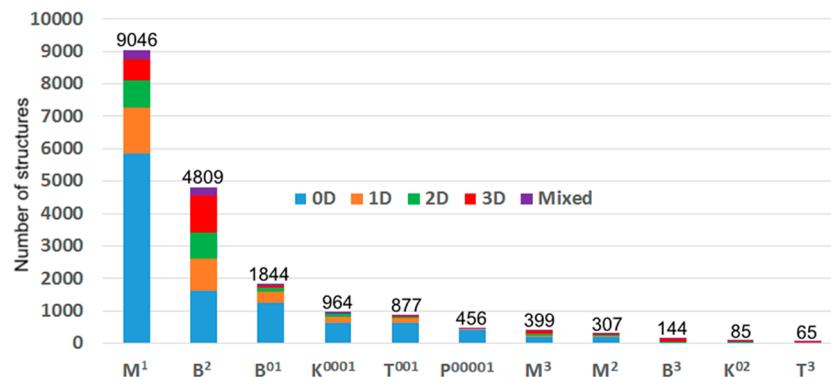


Figure 10. Distribution of coordination modes of ligands depending on the periodicity of the 6613 cyano-containing complexes. The notation used for the coordination modes¹⁰⁹ is described in the Supporting Information.

= Me, Ph, where the tin atom coordinates two cyano groups in the apical positions of a trigonal bipyramidal, occurs, for example, in framework $((n\text{-C}_5\text{H}_{11})_4\text{N})_2[\{\text{Me}_3\text{Sn}\}_4\{\text{Fe}(\text{CN})_6\}_2]\cdot\text{H}_2\text{O}$ [QALWUV]¹²⁰ (Figure 13d) or in 2-periodic $[\text{Fe}(\text{CN})_6\{\text{SnPh}_3\}_2\{\text{SnPh}_3(\text{H}_2\text{O})\}]\cdot 2\text{MeCN}$ [TINDUP].¹³⁰ A sim-

ilar lead-containing spacer, $[\text{PbMe}_3]^-$, joins $[\text{Ru}(\text{CN})_6]^{4-}$ anions into layers in $[\text{Ru}(\text{CN})_6\{\text{Me}_3\text{Pb}\}_2\{\text{Me}_3(\text{H}_2\text{O})\text{Pb}\}_2]$ [LEMDIQ].¹³¹ Unlike $\{\text{M}(\text{CN})_2\}$, these spacers are much more bulky and usually can prevent the formation of porous cyanometallates.

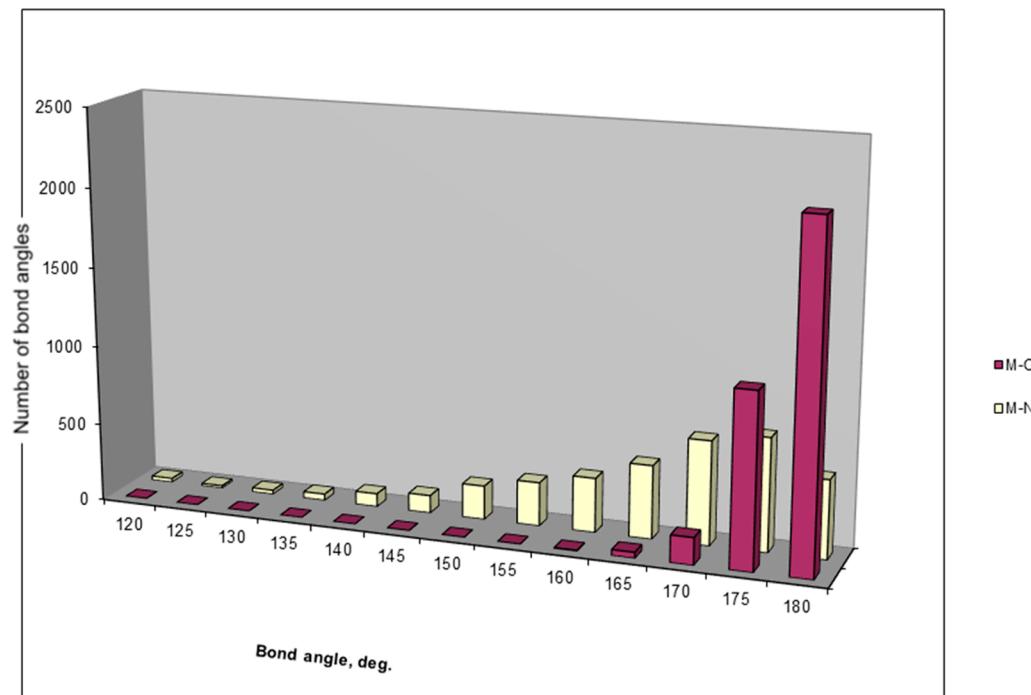


Figure 11. Distribution of 3465 M–N–C and M–C–N bond angles over 1478 *d* metal cyano-containing complexes.

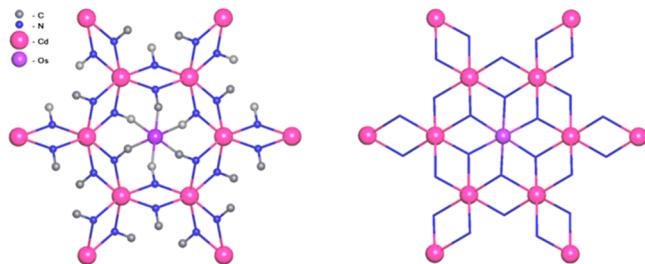


Figure 12. A fragment of the crystal structure of $\text{Cd}_2[\text{Os}(\text{CN})_6]$ [417821]¹¹² with $\mu_3\text{-CN}$ ligands (left) and the resulting underlying net 3,6,6T20 (right).

4.2.1.4. Other spacers. Other spacers are mostly presented by scattered examples. The lantern-type binuclear carboxylates of platinum-group metals $\{\text{M}_2(\mu\text{-OOCR})_4\}$ are worth mentioning as rigid linear spacers, owing to their capability to coordinate two cyano groups, such as, for example, $\{\text{Ru}_2(\mu\text{-OOCMe})_4\}^+$ in 2-periodic $[\text{Ni}(\text{CN})_4\{\text{Ru}_2(\mu\text{-OOCMe})_4\}_2]$ [ORAPUT]¹³² or $\{\text{Ru}_2(\mu\text{-OOC})_4\}^{3+}$ in 3-periodic $[\text{Co}\{\text{Ru}_2(\text{HCOO})_4(\text{CN})_2\}_3]$ [OGIHUI]¹²³ (Figure 13g). In other cases, the spacer can be nonlinear. For example, the crystal structure of $[\text{Mo}\{\text{Li}(\text{dmf})_2(\text{CN})_2\}_3]$ [XIGWUF]¹²⁴ (Figure 13h) contains the $\{\text{Li}(\text{dmf})_2(\text{CN})_2\}$ spacer with Li^+ being tetrahedrally coordinated to two O atoms of two dimethylformamide ligands and two N atoms of two cyano groups. The bond angle (C)N–Li–N(C) of 120.75° provides a peculiar bent system of chemical bonds that forms a framework. Such voluminous and extended spacers drastically and unpredictably influence the resulting framework topology (see below).

4.2.2. Nodes and coordination figures. In this section, we summarize the typical nodes in cyanometallate frameworks, both mono- and polynuclear. In the underlying nets of complex cyanometallates, two types of mononuclear nodes are found.

4.2.2.1. Transition metal atoms. A mononuclear cyano complex can act as a node if more than two cyano groups are

donated for the network extension. Otherwise, the complex can be regarded as a spacer like the aforesaid linear species $\{\text{M}(\text{CN})_2\}$ ($\text{M} = \text{Ag}, \text{Au}, \text{Cu}, \text{Hg}$; Section 4.2.1.2). The geometry of the coordination environment in $[\text{M}(\text{CN})_n]^{q-}$ ($n = 2\text{--}8$) was discussed in detail by Dunbar,¹ Sieklucka et al.,¹² and Larionova et al.¹³³ In all complexes, the metal cation coordinates carbon atoms of cyano groups, which results in stability of such complex groups in the solution. In the simplest case, the $[\text{M}(\text{CN})_n]^{q-}$ anion furnishes all cyano groups for the network extension via coordination of all nitrogen atoms to the M' metal ions. The resulting M–C–N–M' fragment is often almost linear (Figure 11), which makes the corresponding coordination figure predictable, owing to its similarity to the coordination polyhedron. Thus, the $[\text{M}(\text{CN})_n]^{q-}$ complexes are widely used as building blocks in the design of three-periodic cyanometallates. On the contrary, the building blocks that include N-coordinated cyano groups are more complicated to be controlled. Anyway, the relations between the geometry of the metal complex and the coordination figure discussed below are generally correct for all mononuclear nodes.

For tricyanometallates, $n = 3$, only a triangular coordination environment is feasible, as in $[\text{Cu}(\text{CN})_3]^{2-}$, a widely used building block in polymeric cyanometallates (Figure 14).

For tetracyanometallates, $n = 4$, a tetrahedral or square coordination environment is typical for the d^{10} and d^8 electron configurations, respectively. In some three-periodic cyanometallates, such as $[\{\text{Mn}(\text{dmala})(\text{H}_2\text{O})\}_2\text{Mn}\{\text{Mo}(\text{CN})_7\}_2]\cdot2\text{H}_2\text{O}$ [VITFEK]¹³⁴ and $[\text{Mn}_2\text{Nb}(1\text{H-}i\text{mid})_2(\text{CN})_8]$ [VOLZUS],¹³⁵ the framework stabilizes an unusual tetrahedral N_4 environment for the Mn^{2+} cation. At hydration, the Mn^{2+} cation coordinates an additional water molecule, causing the magnetic properties of the complex to change.¹³⁶

Two coordination polyhedron types, a square pyramid (for example, in $\text{Li}_3[\text{Co}(\text{CN})_5]\cdot x(\text{dmf})$ with $x = 2$ [ZIHTIT] or $x = 4$, [ZIHTEP]),¹³⁷ and a trigonal bipyramidal (for example, in

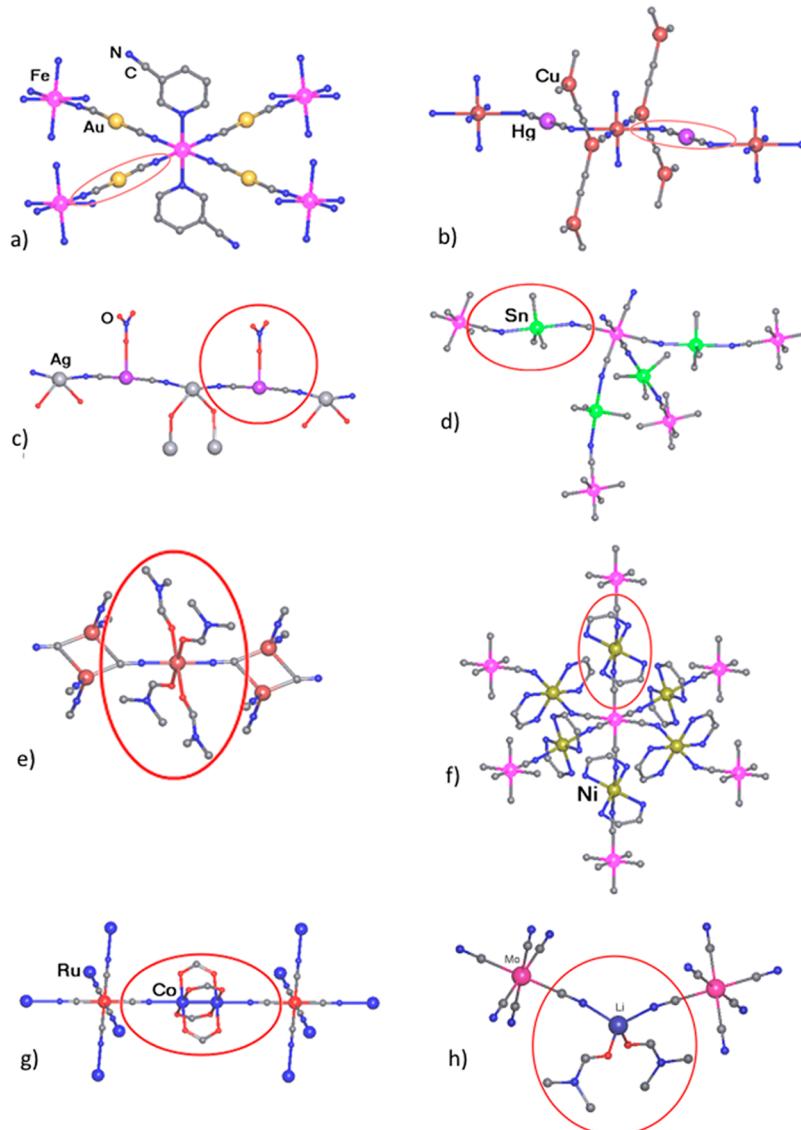


Figure 13. Spacers $M(CN)_2$ and $\{M(CN)_2L_n\}$ in crystal structures: (a and b) $M(CN)_2$ in (a) $[Au_6Fe_3(\mu_2-CN)_{12}(3-pyCN)_6] \cdot 2H_2O$ [WAHMEY]¹¹⁹ (underlying net 4-c nbo) and (b) $[Cu_3(CN)_4(NH_3)_2Hg(CN)_2]$ [172069] (3,4-c tfc);¹¹⁴ (c) $M(CN)_2L$ in $[Hg(CN)_2AgNO_3(H_2O)_2]$ [31920] (6-c pcu);¹¹⁵ (d) $M(CN)_2L_3$ in $(n-C_8H_{11})_4N_2[Fe_2Sn_4(n^2-CN)_8(CN)_4Me_{12}] \cdot 2H_2O$ [QALWUV] (4-c dia);¹²⁰ (e and f) $M(CN)_2L_4$ in (e) $[Cu_5(dmfs)_4(CN)_6]$ [DOLXOR]¹²¹ (6-c rob) and (f) $[FeNi_3(CN)_6(en)_6](PF_6)_2$ [NOBLOF]¹²² (6-c pcu);¹²² (g) $M_2(CN)_2L_4$ in $[CoRu_6(HCOO)_{12}(CN)_6]$ [OGIHUI]¹²³ and (h) bent $M(CN)_2L$ in $[Mo(Li(dmfs)_2(CN)_2)_3]$ [XIGWUF]¹²⁴ (6-c pcu).

nonpolymeric $(Cr(en)_3)[Ni(CN)_5] \cdot 1.5H_2O$ [EDCRCN]),¹³⁸ are typical for $n = 5$.

A group of hexacyanometallates is the most populated, since the $[M(CN)_6]^{q-}$ anions with $M = Fe, Co, Ni, Cr, Ru$, and Os and $q = 2$ and 3 are a part of abundant and well-studied Prussian Blue analogs. An unusual anion $[Mo(CN)_6]^{3-}$ is found in $\{\{Li(dmfs)_2\}_3Mo(CN)_6\}$ [XIGWUF].¹²⁴ In all cases, the metal cations have an octahedral environment.

Heptacyanometallate complexes $[M(CN)_7]^{q-}$ are known for $M = V, Mo$, and Re. The $[V(CN)_7]^{4-}$ anion that was once found in $K_4[V(CN)_7] \cdot 2H_2O$ ¹³⁹ has never appeared in three-periodic cyanometallates. Among all the coordination polyhedra with seven vertices,¹⁴⁰ only a capped trigonal prism and, rarely, a pentagonal bipyramidal are revealed in three-periodic cyanometallates. The latter polyhedron type is the case for $[Re(CN)_7]^{3-}$ in $[Re_2Mn_4(H_2O)_{10}(CN)_{14}] \cdot 6H_2O$ [WUWLOP].¹⁴¹ The distorted pentagonal bipyramidal was reported to

be a coordination polyhedron of Mo^{III} in the layered $K_2Mn_3(H_2O)_6[Mo(CN)_7] \cdot 6H_2O$ [280015].¹⁴²

Coordination number 8 is realized in the anions $[M(CN)_8]^{4-}$, $M = Nb, Mo, W$. The rhenium analogue $[Re(CN)_8]^{3-}$ occurs only in molecular cyanometallates, for example, in $[(MeOH)_{24}Mn_9Re_6(CN)_{48}]$ [WEJSUA].¹⁴³ Square-antiprismatic or bicapped-trigonal-prismatic coordination environments were found in a number of three-periodic cyanometallates, for example, in $[(Mn_2(\mu-ac)(H_2O)_2)Mo(CN)_8] \cdot 2H_2O$ [TOHTIU],¹⁴⁴ and $[(Mn_2(H_2O)_2(2,2'-bpym)M(CN)_8)]$, $M = Nb, Mo, W$ [HIWKOO, HUSGUX, HUSHAE],^{145,146} respectively. An almost regular trigonal dodecahedron (*aka* snub disphenoid or dodecadeltahedron) $[Mo(CN)_8]^{2-}$ was revealed for the molybdenum ion, which lies on either the 2-fold or 4-fold axis in the crystal structures of $\{\{ML_n\}_2Mo(CN)_8\}$, $M = Cu, Ni; L$ are substituted tetra- or hexa-azacyclotetradecane [MUGFOK, VOHTES, NEW-

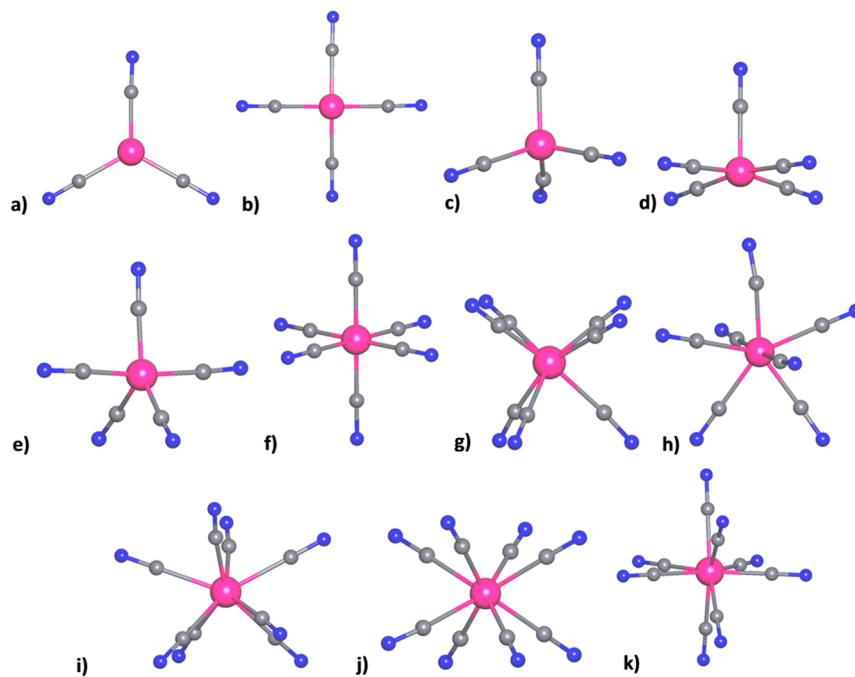


Figure 14. Cyanometalate anions $[M(CN)_n]^{q-}$ representing different coordination polyhedra: (a) triangular, $n = 3$; (b) square and (c) tetrahedral, $n = 4$; (d) square-pyramidal and (e) trigonal-bipyramidal, $n = 5$; (f) octahedral, $n = 6$; (g) capped trigonal-prismatic and (h) pentagonal-bipyramidal, $n = 7$; (i) bicapped trigonal-prismatic, (j) square antiprismatic, and (k) trigonal-dodecahedral, $n = 8$.

QIQ],^{147–149} $n = 1$, or cyclohexanediamine [NULMAJ],¹⁵⁰ $n = 2$.

4.2.2.2. Mononuclear complexes of *d* metals and lanthanides with terminal ligands. The complexes ML_n , where L is a terminal ligand, are structurally diverse, owing to almost unlimited variation of L . We will restrict ourselves to the most important and widespread examples of C- and N-coordinated complexes. First, the nitroprusside $[Fe(CN)_5NO]^{2-}$ ion, where the iron(II) is in a distorted octahedral environment, falls into this category. When all five cyano groups contribute to the network extension, a linear fragment $\{FeNO\}$ becomes a node of the underlying net. The nitroprusside-based cyanometallates possess spin-crossover that attracts to them a sustained interest as to potentially photoswitchable materials.²⁰ The cationic part of *d-f* cyanometallates, $\{Ln(H_2O)_n\}^{3+}$, $n = 2, 3$, also belongs to this group. The coordination environment of the Ln^{3+} cations is square-antiprismatic ($n = 2$) or tricapped trigonal-prismatic ($n = 3$), owing to six additional nitrogen atoms of the cyano groups. Nitroprusside can also generate 2-periodic structures, as happens in the case of its copper(II) salt, $Cu[Fe(CN)_5NO] \cdot 2H_2O$ [414022],¹⁵¹ where Cu^{2+} cations coordinate four N atoms in equatorial positions and two water ligands in the axial ones.

The cyano groups in pure cyano complexes can also be terminal, in particular, in octacyano complexes $[M(CN)_8]^{q-}$. In this case, the complex group $\{M(CN)_m\}$, with m being a number of terminal cyano groups, corresponds to a $(8 - m)$ -coordinated node.

Mononuclear cyano complexes are a convenient example to illustrate how the coordination number of a metal atom correlates with the geometry of the corresponding node and its coordination figure in the underlying net.

If m out of n cyano groups are terminal, the coordination figure has $n - m$ vertices and corresponds to a coordination polyhedron with m vertices removed. However, the coordina-

tion figure can be geometrically distorted compared to the coordination polyhedron if some cyano groups are tilted (Figure 11). However, such distortions are rare, since the M-C-N-M' fragment tends to be linear. For example, hexacyanoferrate anion $[Fe(CN)_6]^{4-}$ can use four equatorial cyano groups ($m = 2$) to coordinate metal cations, which results in square planar nets, as in $[\{Cd(en)_2\}_2Fe(CN)_6]$ [DAZMAT].¹⁵² Furthermore, the 2-periodic structure can also be formed when the coordination figure of $[Fe(CN)_6]^{4-}$ is not square planar but dispheoidal, as in the isostructural $[\{Ln(Me_2SO)_2(H_2O)\}_2Fe(CN)_6]$ ($Ln = Er, Gd$) [CUZGAG, CUZGUA].¹⁵³ The layered structure can be formed also in the case of $m = 3$, as in $[\{Ln(dmf)_2(H_2O)_3\}_2Fe(CN)_6]$ ($Ln = Er, Dy$) [CUZHIP, CUZHOV],¹⁵³ and even if $m = 0$, as in $[Sn_2Fe(CN)_6]$ [51494]¹⁵⁴ and $[Zn_2Fe(CN)_6(H_2O)_5]$ [262668].¹⁵⁵ In the latter two cases, all CN groups of $[Fe(CN)_6]^{4-}$, as in Prussian Blue analogs, coordinate the Sn^{2+} and Zn^{2+} cations but result in a layered structure, not a framework. Different m can even coexist in the same 2-periodic structure. A good example is $[\{CuL_2\}_3\{Co(CN)_6\}_2] \cdot 4H_2O$ ($L = N$ -ethylene-1,2-diamine) [LEHLEQ01],¹⁵⁶ where one $[Co(CN)_6]^{4-}$, a close analog of hexacyanoferrate, with $m = 4$, plays the role of a linear bulky spacer, while the other one, with $m = 2$, coordinates the $\{CuL_2\}^{2+}$ groups by four equatorial cyano ligands.

Tetracyano complex $[M(CN)_4]^{q-}$ degenerates to a bent spacer at $m = 2$ or to a terminal group at $m = 3$. If $m = 1$, the resulting three-coordinated node has a trigonal-pyramidal (Ψ -tetrahedral)¹⁵⁷ coordination figure. An indirect analogy arises here to coordination polyhedra of atoms with a stereoactive lone pair, which can be treated as a ligand blocking the network extension. We distinguish this coordination figure from a triangle to stress its nonplanar geometry, which may dictate the topology of the underlying net. Thus, in $[Cu_2(en)_4(CN)(H_2O)][Cu_2Zn_2(CN)_9]$ [TIFWIP],¹⁵⁸ half of the $[Zn(CN)_4]^{2-}$

Table 3. Coordination Polyhedra and Coordination Figures in the $[M(CN)_8]^{4-}$ ($M = Nb, Mo, W$) Cyano Complexes^a

Formula	Reference	m	Coordination polyhedron	Coordination figure	Underlying net topology
$[(Mn(H_2O)_3(Mn(H_2O)_2)_3(W(CN)_8)_4] \cdot 14H_2O$	[280281] ¹⁶²	1	bicapped trigonal prism	capped trigonal prism	4,4,4,5,5,6,7,7,7T1
$[Mn_2Nb(1H-imid)_2(CN)_8]$	[VOLZUS] ¹³⁵	1	square anti-prism	capped trigonal prism	3,4,7T7
$[(Mn(H_2O)_3(Mn(H_2O)_2)_3(W(CN)_8)_4] \cdot 14H_2O$	[280281] ¹⁶²	2	bicapped trigonal prism	octahedron	4,4,4,5,5,6,7,7,7T1
$[Mn_2(H_2O)_2(2,2'-bpym)M(CN)_8]$, $M = Nb, Mo, W$	[HIWKOO] ¹⁴⁵ [HUSGUX, HUSH-AE] ¹⁴⁶	2	bicapped trigonal prism	trigonal prism	4,6T9 in the standard representation; 6-c pcu in the cluster representation
$[Cd_2(NH_3)_6Mo(CN)_8] \cdot H_2O$	[410311] ¹⁶⁵	2	square anti-prism	distorted pentagonal pyramid	3,3,6T27
$[Mn_2(H_2O)_4(pzdo)Nb(CN)_8] \cdot 7H_2O$	[HIWKII] ¹⁴⁵ [MOJJUR, JEMBUZ, 281480, 249356] ^{164,166-168}	2	square anti-prism	octahedron	4,6T14 and 5-c bnn [HIWKII], 3,6-c ant [MOJJUR, JEMBUZ], 4,4,6T1 [281480], 5,6T18 [249356]
$[M_3W_2(Pym)_2(H_2O)_4(CN)_16] \cdot Pym \cdot 2H_2O$, $M = Mn, Co$	[FANQER, NEKBEL] ^{169,170}	3	bicapped trigonal prism	square pyramid	4,ST7 in the standard representation; 4,8-c scu in the cluster representation
$[M_2Cu_4(CN)_16(en)_6] \cdot 8H_2O$, $M = Mo, W$	[AGOGIM, AFUQOH] ^{159,160}	3	square anti-prism	square pyramid	3,ST1
$[Nd(H_2O)_8][Nd_3Mo_3(CN)_{24}(MeOH)_{12}] \cdot 8MeOH$	[YEGHIC] ¹⁷¹ [HIYYEU, MIJ-MAU] ^{172,173}	4	square anti-prism	tetrahedron	4-c sod [YEGHIC], 4-c dia [HIYYEU, MIJ-MAU]
$\{Ni(Et_2-[14]ane-N_4)\}_2Mo(CN)_8] \cdot 8H_2O$	[MUGFOK] ¹⁴⁷ [WUQRAC, VOHTES, NEWQIQ, NULMAJ, KIJQUQ] ^{148-150,174,175}	4	trigonal dodecahedron	tetrahedron	4-c dia [MUGFOK, VOHTES, NULMAJ, KIJQUQ], 4-c ics [WUQRAC], 4-c neb [NEWQIQ]

^aPictures of the coordination polyhedra and coordination figures are given in the Supporting Information, part 2.

anions use three out of four cyano groups to bind copper ions and to extend the framework. The resulting underlying net is based on tetrahedral {Zn} and trigonal-pyramidal {ZnCN} nodes. Analogously, the latter nodes can be expected to form the frameworks based on any tetrahedral $M(CN)_3L$ complexes.

The examples of five-coordinated nodes based on C-coordinated M cyano complexes are quite rare. Among $[M(CN)_5]^{q-}$ pentacyanometallates, only the aforementioned $[Co(CN)_5]^{3-}$ anions are found to form three-periodic coordination polymers with all five cyano groups being involved in the network extension. Among similar N-coordinated fragments, the Cu(II) complexes showing Jahn–Teller distortion are worth mentioning. The Cu^{2+} coordination polyhedron in $[Cu(NC)_5]^{3-}$ is a square pyramid, and the coordination figure follows this geometry, for example, in the nitroprusside-based framework $[CuFe(CN)_5NO]$ [414021].¹⁵¹ If a chelating ligand distorts the Cu(II) coordination polyhedron as in $[MCu_2(CN)_8(en)_3] \cdot 4H_2O$, $M = Mo$ [AGOGIM],¹⁵⁹ or W [AFUQOH],¹⁶⁰ the coordination figure of the $\{Cu(en)\}$ node degenerates to a trigonal pyramid, $m = 2$. In addition to the tetrahedral and octahedral coordination environments, a trigonal bipyramidal is found for the pentacyanocadmate anion with mixed N- and C-coordinated cyanide ligands in $(Me_2bipy)[Cd_5(CN)_{12}] \cdot 1-BuOH$ [MOD-MIB].¹⁶¹

In octahedral complexes $[M(CN)_5L]^{q-}$, such as nitroprusside ($L = NO$, $m = 1$), the square-pyramidal coordination figure is typical. With two terminal ligands ($m = 2$), both possible coordination figures, a dispphenoid and a square, are found. $\{Mn(H_2O)_3\{Mn(H_2O)_2\}_3\{W(CN)_8\}_4\} \cdot 14H_2O$ [280281]¹⁶² comprises octahedral *cis*- $\{Mn(NC)_4(H_2O)_2\}$ fragments that give rise to dispphenoidal nodes. In $[(Cu(H_2O)_2)_2Mo(CN)_8]$ [240716],¹⁶³ the *trans*- $\{Cu(NC)_2(H_2O)_2\}$ unit with a square-bipyramidal environment of the copper atom results in a plane-squared coordination figure. If $m = 3$, T shaped coordination figures act as nodes, like the $\{Mn(H_2O)_2(imid-3-yl)\}$ node in $[Mn_2Nb(imid-3-yl)_2(H_2O)_4(CN)_8] \cdot 4H_2O$ [MOJJUR].¹⁶⁴ The

$m = 4$ results in degeneration of the $\{M(CN)_2L_4\}$ fragment to a spacer.

In most cases, the $[Mo(CN)]^{4-}$ anions supply all their cyano groups for the network extension. The same concerns the solitary example of the $[Re(CN)]^{3-}$ anion in $\{Mn(H_2O)_5\}_2[Re(CN)_7]_2 \cdot 6H_2O$ [WUWLOP].¹⁴¹ The coordination polyhedron of M and the resulting coordination figure can be treated as a slightly distorted capped trigonal prism or a pentagonal bipyramid. In $(tma)_2\{Mn(H_2O)_3\{Mo(CN)_7\}_2\} \cdot 2H_2O$ [IFUXOW]¹³³ and $\{Mn(dmala)\}_2Mn\{Mo(CN)_7\}_2 \cdot 4H_2O$ [VITFEK],¹³⁴ one of the cyano groups of the $[Mo(CN)]^{4-}$ anion is terminal, $m = 1$. In both structures, the coordination polyhedron of the molybdenum ion is a capped trigonal prism that transforms into a distorted trigonal-prismatic coordination figure.

The most numerous differences between coordination polyhedra and coordination figures are observed in octacyanometallates, $n = 8$. For instance, in the three-periodic frameworks composed of $[M(CN)_8]^{4-}$, $M = Nb, Mo, W$ (Table 1), the number of terminal cyano groups varies in the range $m = 1-4$, which results in coordination figures with $8 - m$ vertices. An interesting example of $\{Mn(H_2O)_3\{Mn(H_2O)_2\}_3\{W(CN)_8\}_4\} \cdot 14H_2O$ [280281]¹⁶² shows how coordination polyhedra can be modified to different coordination figures. Among crystallographically different $[W(CN)_8]^{4-}$ anions, three have $m = 2$, and one has $m = 1$. The resulting $\{W(CN)\}$ ($m = 1$) and $\{W(CN)_2\}$ ($m = 2$) nodes of the underlying net bear capped-trigonal-prismatic and octahedral coordination figures, respectively (Table 3). In other complexes with $m = 2$, the coordination figure is either octahedral (Table 3) or intermediate between an octahedron and a trigonal prism, as in $\{Mn_2(H_2O)_4(pzdo)\}\{Nb(CN)_8\} \cdot 7H_2O$ [HIWKII].¹⁴⁵

4.2.2.3. Polynuclear and cluster nodes. Besides the mononuclear complexes, polyatomic groups comprising the metal ions that coordinate chelating ligands and more than two cyano groups can also play the role of nodes. We subdivide the polyatomic groups by their chemical nature into polynuclear and cluster ones. In three-periodic cyanometallates, the

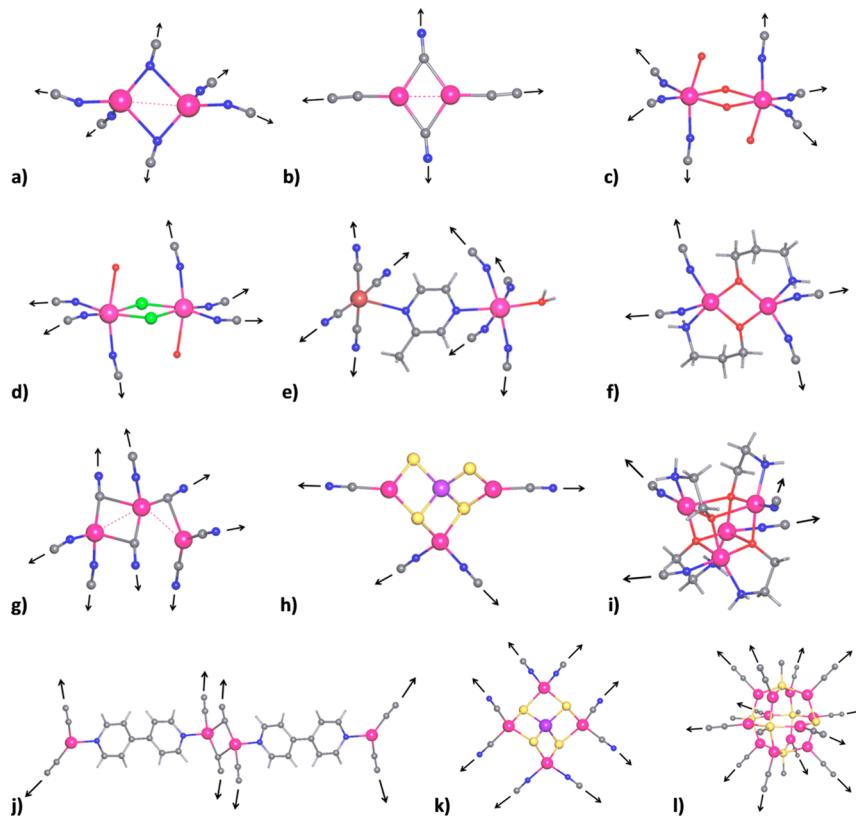


Figure 15. Selected examples of polynuclear complexes acting as nodes: (a–f) binuclear (a) $\{Ag_2\}$ in $(Ag(NH_3)_2)[Ag_2Fe(CN)_6]$ [64627] (6-c pcu in the cluster representation),¹⁸¹ (b) $\{Cu_2\}$ in $[Cu_3(2,6-pym(NH_2)_2)(CN)_3]$ [TIRBEC] (3,4-c fsh-3,4-P2₁/c in the cluster representation),¹⁷⁹ (c) $\{Mn_2(\mu\text{-}H_2O)_4\}$ in $[Mn_2(H_2O)_4Ru(CN)_6] \cdot 4H_2O$ [26216] (6-c pcu in the cluster representation; 4,6T52 in the standard representation),¹⁸⁷ (d) $\{Cd_2(H_2O)_2(\mu\text{-}Cl)_2\}$ in $(Cu(en)_2)[(Cd_2(H_2O)_2Cl_2)Cu_2(CN)_6]$ [XUMCEO] (6-c pcu; 3,4,4T111),¹⁷⁶ (e) $\{NiCd(H_2O)(2mpz)\}$ in $[CdNi(H_2O)(2mpz)(CN)_4]$ [NOQGIK] (6-c acs; 5-c noy),¹⁸⁸ and (f) $\{Cu_2(\mu\text{-}pa)_2\}$ in $[Cu_4Ni_2(pa)_4(CN)_8]$ [XALTIO] (4,4,4T18; 3,3,4,4T26);¹⁸⁹ (g) trinuclear $\{Cu_3\}$ in $[Cu_4(NH_3)_2(H_2O)(CN)_5]$ [16460] (7-c sev);¹⁹⁰ (h–j) tetranuclear (h) $\{Cu_3WS_4\}$ in $(Bu_4N)_2[Cu_3WS_4(CN)_2]$ [YIYYUB] (4-c dia),¹⁹¹ (i) $\{Cu_4(\mu_3\text{-}hea)_4\}$ in $[Cu_4(\mu_3\text{-}hea)_4Mo(CN)_8]$ [JIXXEU] (4-c sra; 3,3,3,4,4,4T1),¹⁹² and (j) $\{Cu(\mu\text{-}bipy)Cu_2(\mu\text{-}bipy)Cu\}$ in $[Cu_2(bipy)(CN)_2]$ [MASMEY01] (6-c pcu; 3,3,4T12);¹⁹³ (k) pentanuclear $\{Cu_4MoS_4\}$ in $(Et_4N)_2[Cu_4MoS_4(CN)_4]$ [WTWQOI]¹⁹⁴ (4-c dia); and (l) dodecanuclear $[Cu_{12}(MeS)_6(CN)_{12}]^{6-}$ in $[Cu_{12}(MeS)_6(CN)_6]$ [JEQVEH] (12-c fcu; 3,4-c tfb).¹⁹⁵

polynuclear complex nodes include transition metal ions connected via bridging ligands. Herein we discuss the most frequent polynuclear complexes acting as the nodes of underlying nets.

a. *Binuclear Cu₂(μ-CN)₂, Ag₂(μ-CN)₂, and Ag₂(μ-NC)₂ complexes.* Among the three-periodic cyanometallates containing polynuclear fragments, the $\{M_2(\mu\text{-}CN)_2\}$ or $\{M_2(\mu\text{-}NC)_2\}$ dimers are rather typical especially for copper(I) and silver(I) cyano complexes (Figure 15a). The $\{M_2X_2\}$ fragment, where X is a donor atom of the bridging cyano groups, is almost flat. The dimers feature short metal–metal distances that justify separation of the $\{M_2\}$ nodes. Each M ion has two additional coordination sites and a tetrahedral environment giving rise to six-coordinated $\{M_2\}$ nodes. The five-coordinated $\{M_2(CN)_5\}$ and four-coordinated $\{M_2(CN)_4\}$ nodes based on the $\{M_2(CN)_6\}$ fragment appear in 3-periodic $[Cu(en)_2]_3[Cd_3\{Cu_2(CN)_6\}_3]$ [XUMCAK]¹⁷⁶ and in 2-periodic $(1,4\text{-}H_2NC_6H_4NH_2)_2[Cu_2(CN)_4]$ [CEXVIM],¹⁷⁷ respectively. Rarely, five- and four-coordinated $\{M_2\}$ nodes occur if one or two M⁺ ions are three-coordinated, as in $[\{Cu_2(dien)(CN)\}\{Cu_2(CN)_3\}\{Cu_2(CN)_2\}]$ [EYACEM]¹⁷⁸ or $[\{Cu_2(2,6-pym(NH_2)_2)(CN)\}_2\{Cu_2(CN)_4\}]$ [TIRBEC]¹⁷⁹ (Figure 15b).

Analysis of the CSD data shows that the distances Cu…Cu vary within 2.31–2.76 Å for all polymeric cyano complexes;

such shortening probably results from weak d¹⁰–d¹⁰ interactions.¹⁷³ The shortest distance is found in the 2-periodic $[Cu_6(tmen)_3(CN)_6]$ coordination polymer [HIWHUQ].¹⁸⁰ In the crystal structures of $(Ag(NH_3)_2)[Ag_2M(CN)_6]$, the $\{Ag_2(\mu\text{-}NC)_2\}$ fragment with Ag…Ag distances of 3.27 Å (M = Fe [64627], Figure 15a) or 3.08 Å (M = Co [64628]) is observed.¹⁸¹ In $[CuAg_2(bapen)(CN)_4]$ [VEGYEM],¹⁸² the distance Ag…Ag of 2.71 Å is rather short. The shortened Ag…Ag contacts close to those in the element silver are quite typical for cyanometallates^{183,184} and therefore can play an important role in crystal engineering.¹⁸⁵ The “aurophilic” Au…Au interactions are the strongest for the 11th group of elements.¹⁸⁶

b. *Fragments based on mononuclear oxo- and chalcogenide molybdenum and tungsten complexes.* When three Cu⁺ ions coordinate $[MQ_4]^{2-}$ anions, where M = Mo, W; Q = O, S, Se, or a $[CpWS_3]^-$ anion, the polynuclear $\{Cu_3MQ_4\}$ or $\{Cu_2MQ_4\}$ fragments result (Figure 15h). The Mo⁶⁺ and W⁶⁺ ions attain a tetrahedral Q₄ environment, while each Cu⁺ ion coordinates two Q atoms. The resulting tetranuclear $\{Cu_3WS_4\}$ and $\{Cu_3(py)CpWS_3\}$ fragments act as nodes in $(Bu_4N)_2[Cu_3WS_4(CN)_2]$ [YIYYUB]¹⁹¹ (Figure 15h) and $[Cu_3(py)CpWS_3(CN)_2]$ [PEKXIN],¹⁹⁶ respectively. A lower coordinated $\{Cu_2MoS_4\}$ fragment was found in 2-periodic $(Et_4N)_3[Cu_4Mo_2S_8(CN)_3] \cdot 2MeCN$ [QENBUH].¹⁹⁷ The

copper(I) cations can coordinate more than one $\{MQ_4\}$ group, assembling, for example, the $\{\text{Cu}_4(\text{MoS}_3\text{O})_2\}$ fragment in 2-periodic $(\text{Et}_4\text{N})_2[\text{Cu}_4(\text{MoS}_3\text{O})_2(\text{CN})_2]\cdot 2\text{NH}_2\text{Ph}$ [MIT-QOW]¹⁹⁸ (Figure 16).

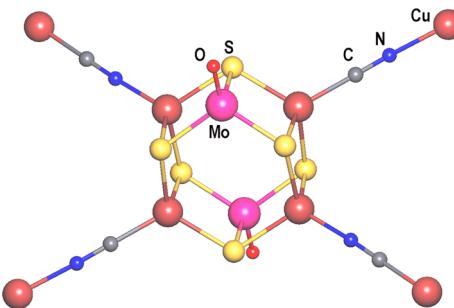


Figure 16. A $\{\text{Cu}_4(\text{MoS}_3\text{O})_2\}$ fragment in 2-periodic $(\text{Et}_4\text{N})_2[\text{Cu}_4(\text{MoS}_3\text{O})_2(\text{CN})_2]\cdot 2\text{NH}_2\text{Ph}$ [MITQOW] (4-c sql in the cluster representation).¹⁹⁸

If the bridging Cu^+ ions coordinate all edges of the Q_4 tetrahedron, the maximal stoichiometry of $\{\text{Cu}_6\text{MQ}_4\}$ is achieved, in particular, in the $[(\text{WS}_4\text{Cu}_6\text{Br}_4)\text{-}(\text{timp})_{8/3}(\text{H}_2\text{O})_{40/3}]_n$ and $[(\text{WS}_4\text{Cu}_6\text{Br}_4)\text{-}(\text{timz})_{8/3}(\text{H}_2\text{O})_{40/3}]_n$ coordination polymers [NUGRIR, NUGROX].¹⁹⁹ In three-periodic cyanometallates, at most, four Cu^+ cations coordinate the $[MQ_4]$ units. The resulting pentanuclear $\{\text{Cu}_4\text{MoS}_4\}$ and $\{\text{Cu}_4\text{WSe}_4\}$ units become eight-coordinate nodes in isostructural $(\text{Et}_4\text{N})_2[\text{Cu}_4\text{MoS}_4(\text{CN})_4]$ [WIWQOI]¹⁹⁴ and $(\text{Et}_4\text{N})_2[\text{Cu}_4\text{WSe}_4(\text{CN})_4]$ [LITHUR]²⁰⁰ (Figure 15k).

c. Polynuclear fragments with noncyanide bridging ligands. In this review, we track the bridging function of the cyano group exclusively, and all noncyanide ligands are considered as parts of the nodes. The chemical diversity of the bridging ligands provides the cyano complexes with polynuclear nodes of any complexity (Figure 15). Binuclear complexes with water or halogen bridging ligands are most typical, for example, $\{\text{Mn}_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2\}$ and $\{\text{Cd}_2(\mu\text{-Cl})_2(\text{H}_2\text{O})_2\}$ nodes with octahedral coordination figures in $[\{\text{Mn}_2(\text{H}_2\text{O})_4\}\{\text{Ru}(\text{CN})_6\}]\cdot 4\text{H}_2\text{O}$ [26216]¹⁸⁷ and $(\text{Cu}(\text{en})_2)\text{-}[\{\text{Cd}_2(\text{H}_2\text{O})_2\text{Cl}_2\}\{\text{Cu}_2(\text{CN})_6\}]$ [XUMCEO], respectively (Figure 15c,d).

Polydentate organic ligands can bind metal ions in both bridging and chelating mode to give a diversity of polynuclear fragments. For example, 3-aminopropanolate in $[\{\text{Cu}_2(pa)\}_2\text{-}\{\text{Ni}(\text{CN})_4\}]$ [XALTIO]¹⁸⁹ is coordinated in a tridentate chelate bridging mode to the copper atoms in a square pyramidal environment (Figure 15f). The resulting $\{\text{Cu}_2(\mu\text{-pa})_2\}$ node is four-coordinated and bears the coordination figure of a square. Another example is the tetra-nuclear cubane-like fragment $\{\text{Cu}_4(\mu_3\text{-hea})_4\}$ with a tetrahedral coordination figure (Figure 15i) found in $[\{\text{Cu}_4(\mu_3\text{-hea})_4\}\{\text{Mo}(\text{CN})_8\}]$ [JIXXEU].¹⁹² Even larger polynuclear complexes were also found, for example, silver-bromide complex node $\{\text{Ag}_6(\mu_4\text{-Br})_3(\mu_3\text{-Br})_2\}$ in 2-periodic $(\text{Et}_4\text{N})_3[\text{Ag}_6\text{Br}_5(\text{CN})_4]$ [EBEMUV]²⁰¹ or Keggin-anion-based $\{\text{PMo}_{12}\text{O}_{37}(\text{OH})_3\text{Nd}(\text{H}_2\text{O})_5\}$ in 2-periodic $[\text{PMo}_{12}\text{O}_{37}(\text{OH})_3(\text{Ln}(\text{H}_2\text{O})_5\{\text{Fe}(\text{CN})_6\}_{0.25})_4]\cdot 12\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}$ [236462], La [262640]).²⁰²

Furthermore, metal atoms can be connected via long spacers such as 2-methylpyrazine in $[\{\text{CdNi}(\text{H}_2\text{O})(2\text{mpz})\}(\text{CN})_4]$ [NOQGIK],¹⁸⁸ via N-containing heterocyclic molecules such as bipyridine in $[\{\text{Cu}_4(bipy)_2(\text{CN})_2\}(\text{CN})_2]$ [MASMEY01],¹⁹³ or via various carboxylates, which are widely used in the chemistry of coordination polymers (Figure 15e,j).

d. Cluster complexes. Cluster complexes, or clusters, are the compounds comprising several *d*-metal ions with short intermetallic distances (about 2.4–2.9 Å), indicative of *M-M* chemical bonding.^{204–207} In contrast to the polynuclear complexes, the polymetallic cluster core is rather chemically stable and usually remains intact in chemical reactions. Among chalcogenide and halogenide clusters, the cyano clusters are indispensable as the centers that are capable of coordinating transition metals to give rise to complexes of any periodicity^{208–222} (Figure 17).

The halogenide and chalcogenide cluster cyano complexes of transition metals had been unknown until the late 1970s. In 1977, W. P. Griffith and coauthors²²³ obtained $(\text{PPh}_4)_4[\text{Re}_4\text{Q}_4(\text{CN})_{12}] \cdot 3\text{H}_2\text{O}$ ($\text{Q} = \text{S}, \text{Se}$), the cluster compound with terminal cyano groups, in a low yield. The cluster anion $[\text{Re}_4\text{Q}_4(\text{CN})_{12}]^{4-}$ proved to be tetrahedral, with each Re_3 face coordinating the chalcogenide anions in a μ_3 fashion and with each Re atom bearing three cyano groups (Figure 17d). The cluster core $\{\text{Re}_4\text{Q}_4\}$ can be regarded as a distorted cube with the metal and chalcogen atoms alternating

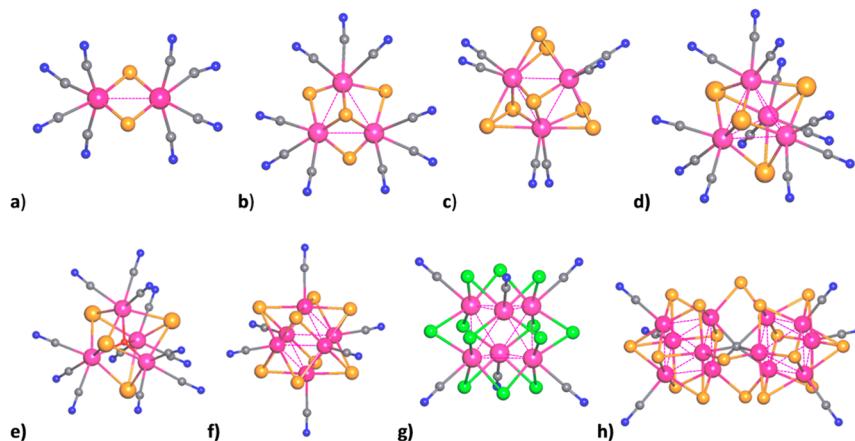


Figure 17. Types of cyano clusters: (a) binuclear $[\text{Mo}_2\text{S}_2(\text{CN})_8]^{4-}$; (b and c) triangular (b) $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-}$ and (c) $[\text{Mo}_3\text{Se}_7(\text{CN})_9]^{2-}$; (d and e) tetrahedral (or cubane-type) $[\text{M}_4\text{Q}_4(\text{CN})_{12}]^{n-}$ ($\text{M} = \text{Re}, \text{Mo}, \text{W}$) and (e) $[\text{M}_4\text{Q}_4(\mu_4\text{-O})(\text{CN})_{12}]^{6-}$ ($\text{M} = \text{Nb}, \text{Ta}$); and (f–h) octahedral (f) $[\text{M}_6\text{Q}_8(\text{CN})_6]^{n-}$ ($\text{M} = \text{Re}, \text{Os}, \text{Mo}, \text{W}$), (g) $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$, and (h) $[\text{Re}_{12}(\mu_6\text{-C})\text{S}_{17}(\text{CN})_6]^{6-/8-}$ cluster anions. Magenta, orange, and green balls stand for M , Q , and halogen atoms, respectively. Dashed lines show possible metal–metal bonds.

in the vertices. For this reason, such clusters are called *cubane-type*.

In the 1980s, A. Muller and coauthors obtained and structurally characterized $K_5[Mo_3S_4(CN)_9] \cdot 3KCN \cdot 4H_2O$, $(Ph_4P)_4[Mo_2S_2(CN)_8] \cdot nH_2O$, and $K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$ cluster cyano complexes.^{224–226} The clusters appeared to be stable in water solutions. Unlike mononuclear cyanometallates, they feature unusual number and spatial arrangement of cyano groups. Since then, the cluster compounds with unique properties have become available for chemists; an opportunity to use them as building blocks suggested itself. However, the first Re, Mo, W, Nb, and Ta cyano cluster coordination polymers were obtained as late as the end of the 1990s. Two scientific groups, of V. P. Fedin and V. E. Fedorov in Russia (working in international collaboration with scientists from UK, France, Korea, and USA)^{227–241} and of C. Perrin in France,^{236,240,242} made a breakthrough by proposing new high-yield synthetic methods for the cyano clusters.

e. *Basic types of cluster cyano complexes.* The chalcogenide and halogenide cluster cyano complexes of M transition metals are known to be based on binuclear (M_2), triangular (M_3), tetrahedral (M_4), or octahedral (M_6) cores of the metal ions coordinating chalcogenide (Q), halogenide (X), or dichalcogenide (Q_2) ligands in a μ_2 , μ_3 , or $\mu_2\eta^2$ (for Q_2) mode^{204–207} (Figure 17). In trinuclear cluster anions (Figure 17b, c), such as $[Mo_3S_4(CN)_9]^{5-}$ and $[W_3TeSe_3(CN)_9]^{5-}$ or $[Mo_3Se_7(CN)_9]^{2-}$ and $[W_3Te_7(CN)_9]^{2-}$, three μ - Q ligands or $\mu_2\eta^2$ - Q_2 ligands, respectively, are coordinated to the metal atoms in addition to the μ_3 - Q ligands. The tetrahedral $\{M_4Q_4\}$ cores (Figure 17d), where M is Mo, W, or Re, have a cubane structure. In similar niobium and tantalum clusters, the core is oxo-centered (μ_4 -O) (Figure 17e) which results in elongated metal–metal distances. The $M\cdots M$ distances of ~ 3.0 Å are found in $[Mo_4Te_4(CN)_{12}]^{7-}$, while even longer distances of about 3.2 Å feature the $[Nb_4Te_4(\mu_4\text{-O})(CN)_{12}]^{6-}$ anion.²²⁶ The octahedral cluster core (Figure 17f) can be represented as an octahedron of the M atoms inscribed into a cube of the Q atoms.²⁴² In an unprecedented $[Re_{12}(\mu_6\text{-C})_S_{17}(CN)_6]^{6-8-}$ cluster anion, two such Re_6 octahedra are joined through a bridging carbon atom and three μ - S ligands²³⁴ (Figure 17h).

All cyano cluster anions are stable in aqueous solution. Many of them (for example, $[Re_6Q_8(CN)_6]^{3-4-}$,^{243,244} or $[M_4Q_4(CN)_{12}]^{6-7-}$, $M = Mo, W$)^{229,230} can be oxidized or reduced, preserving the geometric characteristics of the cluster core. Selective two-step oxidation of the bridging μ - S ligands of $[Re_{12}(\mu_6\text{-C})S_{17}(CN)_6]^{6-}$ in aqueous solution results in formation of μ - SO_2 and μ - SO_3 ligands while the Re_{12} metal core and cyano groups remain untouched.²⁴⁵

The cluster cyano complexes are attractive for crystal engineering since they can be directly introduced into the reaction, thereby being true building blocks. In contrast, polynuclear complexes are usually assembled *in situ* that require specific conditions. Notwithstanding quite different roles in the synthesis and design of the coordination polymers, polynuclear and cluster cyano complexes often give rise to topologically similar nodes in the resulting frameworks. For this reason, in this review, we will make no special distinction between them, except for some cases.

5. OVERALL STRUCTURE MOTIFS IN CYANOMETALLATES

In the previous section, we have considered how the chemical constituents (complexing atoms and ligands) transform to the structural components (nodes and spacers), which predetermine the local topological properties (coordination figures) of the cyano complexes. Below we analyze the relations between the local and overall topological characteristics of the structural motifs in the cyanometallates.

5.1. Most typical extended motifs

According to Table 4 the most abundant topological types of three-periodic cyanometallates are primitive cubic lattice (**pcu**),

Table 4. Occurrence of Most Abundant Nets in the 557 Three-Periodic Cyanometallates

Underlying net	Occurrence	Coordination figures in the maximum-symmetry embedding	Other coordination figures that can be adopted via distortion
6-c pcu	116; 20.8%	octahedron	
4-c dia	57; 10.2%	tetrahedron	disphenoid, distorted square pyramid
6-c nia	47; 8.4%	octahedron + trigonal prism	
4-c pts	18; 3.2%	square + tetrahedron	square + disphenoid
5-c noy	17; 3.1%	square pyramid	
6-c acs	16; 2.9%	trigonal prism	
4,6-c stp	16; 2.9%	square + octahedron	square pyramid + octahedron
4,8-c scu	15; 2.7%	square + square antiprism	
4-c cds	14; 2.5%	square	
4-c qtz	8; 1.4%	tetrahedron	disphenoid
3,6-c rtl	8; 1.4%	triangle + octahedron	trigonal pyramid + octahedron

diamond net (**dia**), and NiAs type (**nia**, Figure 6); 39.5% of the cyano complexes fall into these three types. The **pcu** topology is so widespread due to numerous Prussian Blue analogs. Note that the **pcu** and **dia** nets contain nodes of the same coordination (*homocoordinated*) in contrast to the *heterocoordinated* **nia** net. The cyanometallates with the heterocoordinated underlying nets are fewer than those bearing homocoordinated nets (173 and 384, respectively, see Table S1). At that, the heterocoordinated nets are represented with 90 topological types; that is, they are more topologically diverse than the homocoordinated ones described with merely 61 types. The diversity in the coordination environment can originate from both different coordination numbers of the metal atoms and different arrangement of the coordination sites if they are, for example, blocked with terminal ligands (see Section 4.2.2). Most topological types of the heterocoordinated nets are scanty, except 3,6-coordinated **rtl**, 4,6-coordinated **stp**, and 4,8-coordinated **scu**, which were found in the 8, 16, and 15 frameworks, respectively.

Interpenetration appears in 96 complexes and is most preferable for the frameworks with 6-coordinated (40 compounds) and 4-coordinated (39 compounds) underlying nets; among them, **pcu** (29 compounds) and **dia** (16 compounds) predominate. A majority of the structures contain 2 (47 compounds) or 3 (32 compounds) frameworks that are ordinarily related by translations (74 compounds, class of interpenetration Ia).²⁴⁶ For the heterocoordinated nets, interpenetration is not characteristic and is realized only for the

Table 5. First Ten Most Abundant Network Topologies in Molecular (0D), Chain (1D), Layer (2D), and Framework (3D) Complexes Containing at Least One CN Group

Topology	No. of structures	Topology	No. of structures	Topology	No. of structures	Topology	No. of structures
0D	4058	1D	1054	2D	748	3D	950
1,4M5-1	705; 17.4%	2C1	794; 75.3%	4-c sql	414; 55.3%	6-c pcu	170; 17.9%
1,6M7-1	666; 16.4%	2,2,4C3	91; 8.6%	3-c hcb	157; 21.0%	4-c dia	89; 9.4%
1,2M3-1	519; 12.8%	3-c 4 ⁴ (0,2)	66; 6.3%	3,6-c kgd	24; 3.2%	6-c nia	65; 6.8%
1,3M4-1	397; 9.8%	2,4C4	7; 0.7%	3,4L13	10; 1.3%	4,6-c fsc	51; 5.4%
1,5M6-1	172; 4.2%	3,5C1	7; 0.7%	4-c 6 ³ Ia	9; 1.2%	5-c noy	20; 2.1%
1,2,2M5-1	77; 1.9%	4-c 3 ⁶ (1,2)	6; 0.6%	3,4L83	8; 1.1%	3,6-c rtl	20; 2.1%
1,8M9-1	59; 1.5%	2,2,3C4	3; 0.3%	3,4-c mcm	6; 0.8%	6-c acs	19; 2.0%
1,2,4M9-2	58; 1.4%	2,4C8	3; 0.3%	3,3L19	5; 0.7%	4-c cds	19; 2.0%
1,2,4M16-1	53; 1.3%	4-c 4 ⁴ (0,4)	2; 0.2%	5-c 4 ⁴ Ia	5; 0.7%	4-c pts	19; 2.0%
1,2,3M7-2	50; 1.2%	2,2,3C6	1; 0.1%	3-c KIa	4; 0.5%	4,6-c stp	16; 1.7%

Table 6. Main Correlations “Chemical Composition–Local Topology–Overall Topology” for the Cyano Complexes with Six-Coordinated Underlying Nets

Node composition	Spacer composition	Extra-framework species	Coordination figure	Underlying net	Interpenetration
$[Ln(H_2O)_3]^{3+}$	$[M(CN)_2]^-$		Trigonal prism	acs	3-fold
$[M_n(L)_m]^{y+}$	CN ⁻	THF, NO ₃ ⁻			
$M^{x+}/[Ln(H_2O)_n]^{3+}$	CN ⁻	M^{x+}, H_2O	Octahedron + Trigonal prism	nia	
$[Re_6Te_8]^{3+} + [La(H_2O)_3]^{3+}$	CN ⁻	H ₂ O			
M^{x+}	CN ⁻	M^{x+}, H_2O	Octahedron	pcu	
	$[M(CN)_2]^-$	M^{x+}, H_2O Bu_4N^+		bcs	3-fold
	compact $[ML_nCN]^-$	(CoCp ₂)		rob	
	voluminous $[ML_nCN]^-$	An^{y-}, H_2O		pcu	
	$[Bu_3Sn(CN)_2]^-$			lcy	
$[M_6Q_8]^{x+}$	compact $[ML_nCN]^-$	H ₂ O		pcu	2-fold
	voluminous $[ML_nCN]^-$	M^{x+}, H_2O		rob	
		$Me_4N^+, MeCN$		rob	
$[M_3(L)_2]^{x+}$	CN ⁻			pcu	2-fold
	CN ⁻ and/or $[M_n(CN)_{n+1}]^-$	$[Cu(H_2O)(en)_2]^+$			

underlying nets with low coordination (3,4), (3,6), (3,8), or (4,6) totally in 10 compounds.

The topology distribution for the framework cyano-containing complexes (Table 5) is quite similar; the same underlying nets **pcu**, **dia**, and **nia** mostly occur (Figures 6, S20–S22). Moreover, in the complexes with a low periodicity (molecular, chain, and layer) the same trend is observed; only a few most simple network topologies are abundant (Figures S2–S19). Below we consider the main factors that influence the overall topology of extended motifs in 557 three-periodic cyanometallates; separately, the relations between them and the low-periodic (chain or layered) cyanometallate polymers will be outlined.

5.2. General relations between coordination figure and framework topology

As was stated above, the overall topology of an underlying net notably depends on the local environment of the structural fragments (complexing atoms, polynuclear complexes, polydentate ligands) corresponding to nodes as well as on the stoichiometry of nodes and spacers. Hence, the shape of the coordination figure significantly restricts feasible underlying net topologies.^{96,105} Note that theoretically the number of possible topologies under specified local topological parameters (coordination number and figure of a node, sizes of shortest rings) is much larger than those found in crystal structures. For

example, the TOPOS TTD collection^{96,98,105} contains more than 750 uninodal three-periodic four-coordinated nets, but only 15 of them have been found in cyanometallates.

The most frequent underlying topologies (**pcu**, **nia**, **acs**, **dia**, etc.) correspond to the most probable combinations of building complex groups, when the local environment of the node in a given net coincides with the most typical (octahedral, trigonal-prismatic, etc.) coordination of metal atoms. Moreover, the preferred underlying topologies are resistant to the framework expansion; they can be retained when replacing metal atoms with clusters or polynuclear complex groups of a specific (strongly predetermined) geometry of coordination. For example, the **pcu** underlying motif is preserved after replacing the nodes with octahedrally coordinated groups. Thus, the required topological type can be obtained by varying the stoichiometry of nodes of the same or different coordinations. To illustrate these general relations between the underlying net topology and the local environment of nodes, an example of six-coordinated underlying nets in 191 frameworks of cyano complexes is presented in Table 6. Despite the fact that the six-coordinated nets are the most preferred (they compose about 34.3% of all three-periodic cyanometallates), they provide a narrow set of **pcu**, **nia**, **acs**, **rob**, **lcy**, 6T13, **bcs**, and **msw** underlying topologies, where the first three are the most abundant (Tables 4, S2).

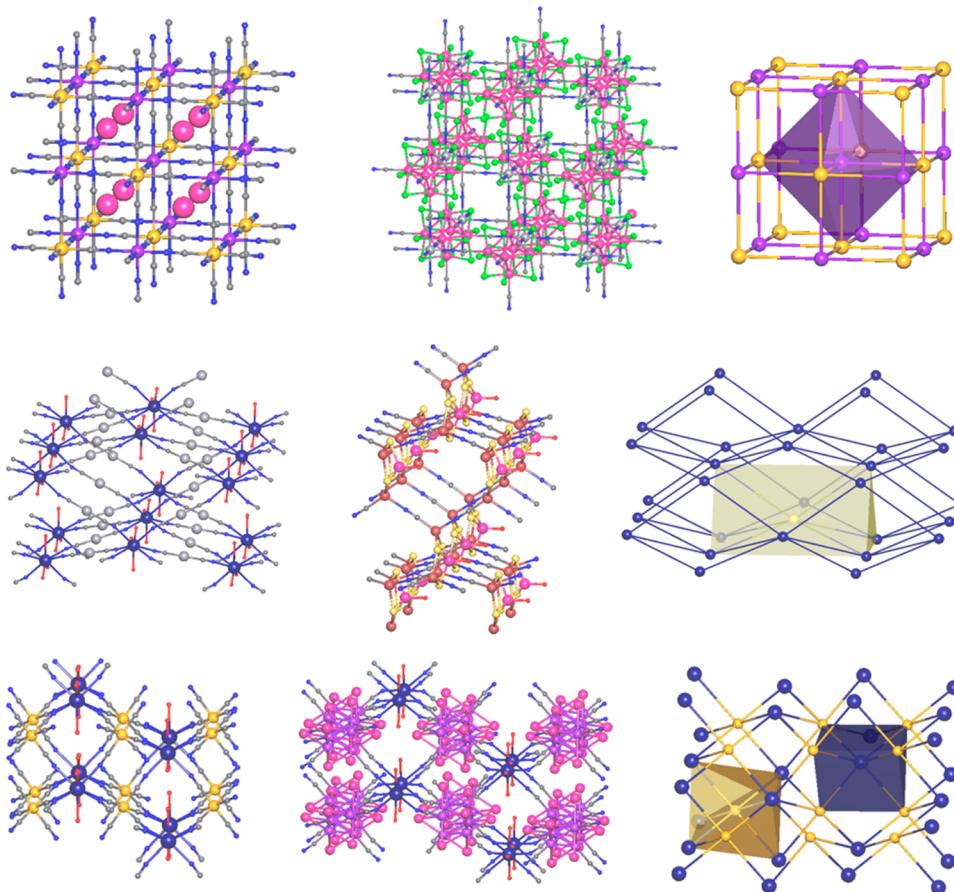


Figure 18. Fragments of the frameworks in the mononuclear cyano complexes and their cluster-expanded analogues as well as the corresponding underlying nets: (top) $K_2Co[Fe(CN)_6]$ [28669],⁵³ $(Me_4N)_2[MnNbCl_{12}(CN)_6]$ [AQEMIS],²⁴⁷ pcu; (middle) $[Ag_3La(CN)_6(H_2O)_3]$ [170986],²⁵⁹ $(Me_4N)_3[Cu_3WOS_3](CN)_3](NO_3)$ [UNABER],²⁵³ acs; (bottom) $[FeM(CN)_6(H_2O)_3] \cdot 2H_2O$ [2581],²⁵⁸ $\{La(H_2O)_3\}Re_6Te_8(CN)_6 \cdot 4H_2O$,²⁵⁶ nia.

The most preferable coordination figure is an octahedron (126 compounds), which can be found for the following types of cyanometallates.

(i) The frameworks based on octahedral coordination figures and connected by *only cyanide bridges* have exclusively the **pcu** underlying topology (Figure 18 top). Many such frameworks are intrinsic for the Prussian Blue analogues.

(ii) In almost all cases, octahedral-coordinated anionic cubane clusters $[W_4Q_4(CN)_{12}]^{x-}$ ($Q = S$ or Te) and octahedral clusters $[Nb_6Cl_{12}(CN)_6]^{x-}$, $[M_6Q_8(CN)_6]^{x-}$ ($M = Re$, Mo , or W ; $Q = S$, Se , or Te) are assembled in **pcu** frameworks if they are connected through the N atoms of the CN groups and the complexing spacers with octahedrally coordinated ions, such as Ga^{3+} [280737],²¹⁷ Mn^{2+} [AQEMIS]²⁴⁷ (Figure 18 top), and Fe^{2+} [HEXQIL],²⁴⁸ or with polynuclear complexes, such as $[Sn_4Me_8O_2]^{4+}$ [CUCPIA],²⁴⁹ $[Cd_2(\mu-H_2O)_2(H_2O)_2]^{4+}$ [87980],²¹⁴ and $[Mn_2(\mu-H_2O)_2(H_2O)_2]^{4+}$ [KUGFAU].²⁵⁰

(iii) In almost all structures with *polynuclear nodes*, the **pcu** topology is realized irrespective of the polynuclear node size. Thus, in six compounds, the **pcu** framework is based on binuclear complex groups $\{M_2(\mu-H_2O)_2(H_2O)_2\}^{4+}$ ($M = Cd$, Mn) and six-coordinated hexacyanometallate anions. In another series of the $[\{Mn_2(2,2'-bipym)(H_2O)_2\}\{M(CN)_8\}]$ ($M = Nb$, Mo , W) compounds [HIWKOO, HUSGUX, HUSHAE],^{145,146} the combination of larger binuclear $\{Mn_2(\mu-2,2'-bipym)(H_2O)_2\}^{4+}$ and mononuclear $\{M(CN)_8\}^{4-}$ complex groups also results in the **pcu** underlying nets. Again, the **pcu** motif

features the system of large tetranuclear $\{Cu_4(\mu_3-I)_2(\mu-CN)_2\}$ species connected by six $\mu-CN^-$ and two μ_4-CN^- spacers in $Cs_2[Cu_4(CN)_4I_2] \cdot H_2O$ [170203] and $[Cu(H_2O)_4]\cdot[Cu_4(CN)_4I_2]$ [170204].²⁵¹

All 16 frameworks with the *trigonal-prismatic coordination* of nodes have the **acs** underlying topology. In 11 frameworks, the trigonal-prismatic coordination figures originate from a trigonal-prismatic environment of the lanthanide atom capped with three terminal ligands (Figure 18 middle). In other cases, the nodes correspond to polynuclear complex groups: $\{Cu_3MOS_3\}$ ($M = Mo$, W , Figure 18 middle) in $(Me_4N)_3[Cu_3WOS_3](CN)_3](NO_3)$ [JOBFAI]²⁵² and $(Me_4N)_3[Cu_3MoOS_3](CN)_3](NO_3)$ [UNABER],²⁵³ $\{CdNi(H_2O)(2mpz)\}$ in $[CdNi(H_2O)(2mpz)-(CN)_4]^{4+}$ [NOQGIK]¹⁸⁸ (Figure 15e), $\{CdNi(H_2O)(ampy)\}^{4+}$ in $[CdNi(H_2O)(ampy)(CN)_4] \cdot thf$ [DEKYUP],²⁵⁴ and $\{Cu_3(Hat)\}$ in $[Cu_3(Hat)(CN)_3] \cdot thf$ [XEKJIH].²⁵⁵

A combination of *octahedral* and *trigonal-prismatic coordination* figures in a 1:1 ratio is typical for the **nia** underlying net that occurs in a series of *d-f*-cyanometallates¹ $Ln[M(CN)_6] \cdot (H_2O)_n$ and $(K,Tl)Ln[M(CN)_6](H_2O)_n$, where Ln are lanthanides, Bi , or Y ; M are Fe , Co , Cr , or Ru ; $n = 0, 0.5$, or 1.5 (Figure 18 bottom). Thus, the *d-f*-cyanometallates and their Bi - and Y -containing analogues cover 45 out of 47 structures with the **nia** topology. Here the *d* metal corresponds to the node with an octahedral coordination figure, while the lanthanide atom has a capped or a tricapped trigonal-prismatic, or tetragonal-antiprismatic environment that provides a

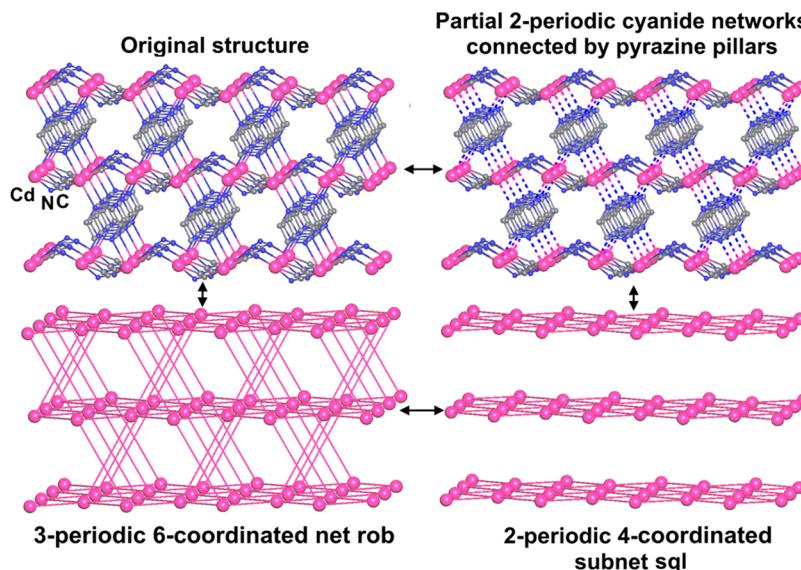


Figure 19. Relation between the overall topology of mixed-ligand $[\text{Cd}(\text{CN})_2(\text{pz})]$ cyano complex [HEHHAD]²⁵⁹ and its two-periodic cyanide-bridged subnet.

Table 7. Occurrence (N) of the Most Abundant Topological Types in the Homoleptic Cyano Complexes

Topology	N	Topology	N	Topology	N	Topology	N
0-periodic	544	1-periodic	15	2-periodic	42	3-periodic	211
1,6M7-1	206; 37.9%	2C1	15; 100%	3-c hcb	25; 59.5%	6-c pcu	91; 43.1%
1,4M5-1	186; 34.2%			4-c sql	11; 26.2%	4-c dia	40; 19.0%
1,2M3-1	101; 18.6%			3,6-c kgd	4; 9.5%	4-c pts	7; 3.3%
1,8M9-1	32; 5.9%			5-c 4 ⁴ Ia	2; 4.8%	3,6,6T20	7; 3.3%
1,7M8-1	7; 1.3%					4,6-c cor	7; 3.3%

Table 8. Most Common Topological Types of Cyanide-Bridged Building Blocks for the 403 Mixed-Ligand Complexes

Topology	N	Topology	N	Topology	N	Topology	N
0-periodic	58	1-periodic	92	2-periodic	131	3-periodic	137
1,2M3-1	26; 44.8%	2C1	82; 89.1%	4-c sql	109; 83.2%	5-c stp	17; 12.4%
1,2,2M5-1	5; 8.6%	3-c 4 ⁴ (0,2)	5; 5.4%	3-c hcb	4; 3.1%	6-c pcu	14; 10.2%
1,4M5-1	4; 6.9%	2,2,4C3	2; 2.2%	3,4L84	3; 2.3%	3,6-c rtl	13; 9.5%

trigonal-prismatic coordination figure with one, two, or three coordination sites (caps) occupied by terminal ligands.

The same combination of coordination figures exists in the $[\text{La}(\text{H}_2\text{O})_3][\text{Re}_6\text{Te}_8(\text{CN})_6]$ ²⁵⁶ framework, which contains both an octahedral cluster $[\text{Re}_6\text{Te}_8(\text{CN})_6]^{3-}$ and mononuclear complex $[\text{La}(\text{H}_2\text{O})_3(\text{CN})_6]^{3+}$ (Figure 18 bottom). The trigonal-prismatic environment is inherited from the tricapped trigonal-prismatic environment of the La^{3+} ion.

5.3. Low-periodic cyanometallates as infinite building blocks for coordination polymers

According to the general statistics (Table 1), cyanide frequently combines with other ligands to form mixed-ligand (or heteroleptic, $\text{CN}^- + L$) complexes; there are 703 3-periodic structures of this type. The additional ligands L can be either terminal ($t\text{-}L$, in 464 structures) or bridging ($\mu\text{-}L$, in 403 structures). It was already discussed above that the $t\text{-}L$ ligands modify the local topology of the cyano complexes, while bridging $\mu\text{-}L$ ligands can extend the nodes. However, if the stoichiometric ratio of $\mu\text{-}L$ ligands in the structure increases, the $\mu\text{-}L$ ligands act as spacers. In most cases, they cannot any longer be regarded as part of the nodes, because they are involved in infinite structural fragments. In other words, with increasing

number of $\mu\text{-}L$ ligands, cyano spacers alone cannot provide a three-periodic structure, the cyano-bridged networks become low-periodic, and the $\mu\text{-}L$ ligands increase the dimensionality of the framework. As was already said above, such compounds cannot be considered as three-periodic cyanometallates but can bear homoleptic cyanometallate motifs of a lower periodicity. Using the topological approach, it is possible to analyze separately the structural role of the $\mu\text{-CN}$ and $\mu\text{-}L$ spacers in the 403 heteroleptic complexes; for this purpose, the edges of the underlying net corresponding to $\mu\text{-}L$ should be ignored. For example, in the crystal structure of the heteroleptic complex $[\text{Cd}(\text{CN})_2(\text{pz})]$, cyano and pz bridging ligands in a 2:1 ratio form a three-periodic 6-coordinated underlying net **rob**. If one ignores the pyrazine spacers, a two-periodic cyano-bridged subnet can be separated (Figure 19), which possesses a 4-coordinated **sql** underlying topology typical for the two-periodic homoleptic cyanometallates (Table 7). Using other $\mu\text{-}L$ ligands to join the **sql** cyanide-bridged sheets, one can obtain many new three-periodic coordination polymers.²⁵⁹

Analyzing in this way all the 403 cyanide structures (Table 1) that contain $\mu\text{-}L$, we have collected all typical cyanide-bridged building blocks, both molecular and polymeric (Table S4, Figure S12–S22). In Table 8, the most frequent topological

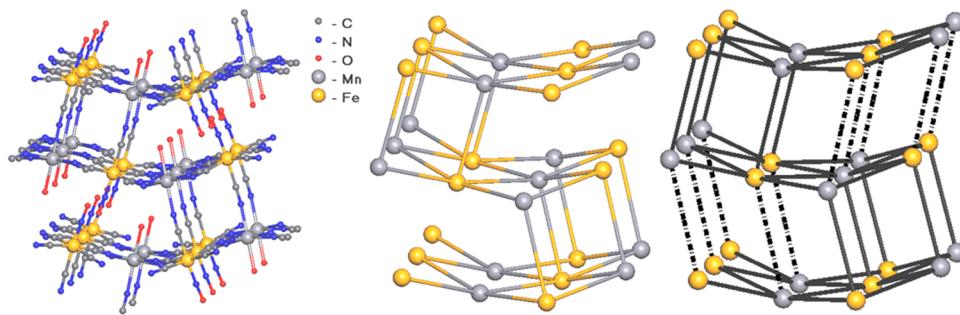


Figure 20. (Left) Framework fragments in $\left[\{\text{Mn}(\text{H}_2\text{O})\}\{\text{Fe}(\text{CN})_5\text{NO}\}\right]\cdot\text{H}_2\text{O}$ [69137];²⁶¹ (middle) the corresponding **noy** underlying net; (right) the **noy** net with additional bonds (dotted lines), which complete it to a **pcu** net.

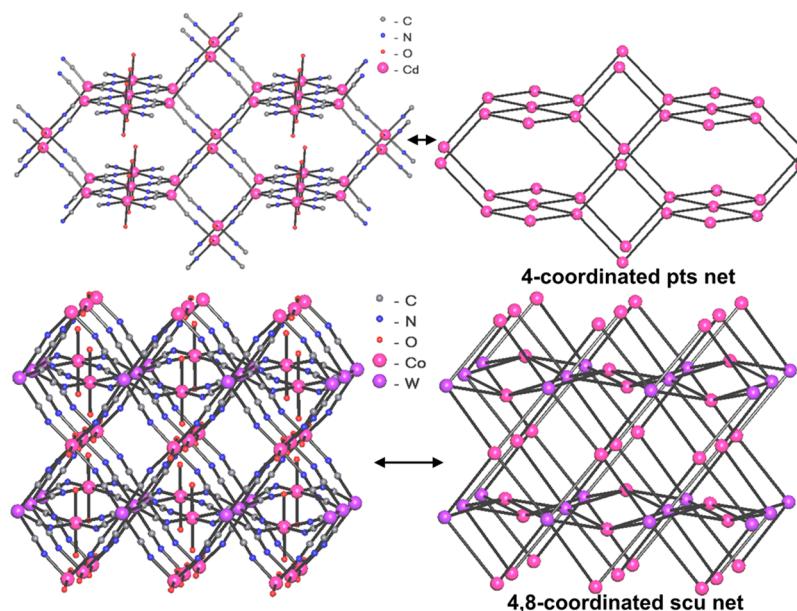


Figure 21. Fragments of frameworks (left) and the corresponding underlying nets (right) in $\left[\{\text{Cd}(\text{H}_2\text{O})_2\}\{\text{Cd}(\text{CN})_4\}\right]\cdot 2(\text{dxn})$ [NINHOH]¹⁰⁴ and $\left[\{\text{Co}(\text{H}_2\text{O})_4\}_2\{\text{W}(\text{CN})_8\}\right]\cdot 4\text{H}_2\text{O}$ [281479].¹⁶⁷

motifs of the cyanide-bridged building blocks are listed. It is noteworthy that their topologies, such as 1,2M3-1, 2C1, **sql**, **stp**, **pcu**, or **rtl** (Figures S12–S22), are also among the most abundant topological motifs both in the homoleptic cyanometallates (Table 7, Figures 6, S2–S10) and in other cyanoo-containing complexes (Table 5). This supports an idea that the cyanide-bridged cyanometallate fragments can serve as extended building blocks in the design of coordination polymers.

5.4. Chemical factors influencing the network topology

5.4.1. Terminal ligands. The complexes containing terminal ligands are quite common for the cyanometallates (234 complexes, 42.0%). Terminal ligands can occupy different numbers of coordination sites that reduce the coordination figure (Figure 5). Below, the most typical groups of such complexes are considered.

5.4.1.1. Complexes with coordination sites blocked by terminal ligands. In particular, nitroprusside $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ -ion falls into this category and results in 5-coordinated underlying nets of a **noy** topology in $\left[\{\text{Fe}(\text{H}_2\text{O})\}\{\text{Fe}(\text{CN})_5(\text{NO})\}\right]\cdot 2\text{H}_2\text{O}$ [71228],²⁶⁰ $\left[\{\text{Mn}(\text{H}_2\text{O})\}\{\text{Fe}(\text{CN})_5(\text{NO})\}\right]\cdot 2\text{H}_2\text{O}$ [69137],²⁶¹ $[\text{M}\{\text{Fe}(\text{CN})_5\text{NO}\}]$ ($\text{M} = \text{Cd, Pb, Mn}$) [109420, 152063, 109421]^{262,263} (Figure 20 left, middle) and other complexes. This net is known to be related to

pcu, which is characteristic for the Prussian Blue analogues (Figures 18 top, 20 right).

5.4.1.2. Complexes formed due to substitution of terminal ligands by cyano groups. Typical examples are aquacyanometallates with 4,8-coordinated **scu** and 4-coordinated **pts** underlying topologies (Figure 21). The complexes of the **scu** topology can be obtained by reaction of $[\text{M}_1(\text{CN})_8]^{4-}$ ($\text{M}_1 = \text{Mo, W, Nb}$) with $[\text{M}_2(\text{H}_2\text{O})_6]^{2+}$ ($\text{M}_2 = \text{Cd, Co, Cu, Fe, Mn}$) in a 2:1 ratio; see, for example, $[\{\text{Fe}(\text{H}_2\text{O})_2\}_2\{\text{Mo}(\text{CN})_8\}]\cdot 4\text{H}_2\text{O}$ [QEBGEJ].²⁶⁴ A reaction of $[\text{M}_3(\text{CN})_4]^{2-}$ ($\text{M}_3 = \text{Cd, Cu, Zn}$) with $[\text{M}_4\text{L}_6]^{2+}$ ($\text{M}_4 = \text{Cd, Cu, Zn}; \text{L} = \text{H}_2\text{O, NH}_3, \text{acetonitrile, pyridine}$) in a ratio of 1:1 leads to formation of a compound with a 4-coordinated **pts** underlying net; see, for example, $[\{\text{Cd}(\text{py})_2\}\{\text{Zn}(\text{CN})_4\}]$ [DULNAA],²⁶⁵ $[\{\text{Cd}(\text{H}_2\text{O})_2\}\{\text{Cd}(\text{CN})_4\}]\cdot 2\text{dxn}$ [NINHOH],¹⁰⁴ $[\{\text{Cd}(\text{NH}_3)_2\}\{\text{Cd}(\text{CN})_4\}]\cdot \text{C}_6\text{H}_6$ [YARYEV].²⁶⁶ In the resulting complexes, the square antiprismatic and tetrahedral coordination polyhedra $[\text{Ln}(\text{CN})_8]^{4-}$ and $[\text{M}_3(\text{CN})_4]^{2-}$ match the coordination figures of the corresponding nodes (Ln and M) in the underlying nets. At the same time, the square coordination figure of the $\{\text{ML}_2\}$ nodes is a result of substitution of four equatorial terminal ligands in the octahedral complexes $[\text{M}_2(\text{H}_2\text{O})_6]^{2+}$ or $[\text{M}_4\text{L}_6]^{2+}$ by bridging cyano groups (Figure 21).

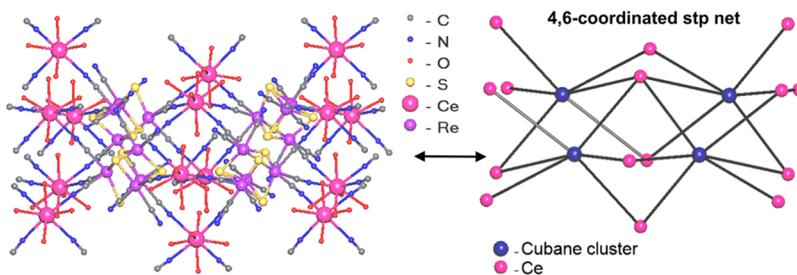


Figure 22. (Left) A fragment of the framework in $[\text{Ce}(\text{H}_2\text{O})_4(\text{H}_2\text{O})_{2/3}\text{Cl}_{1/3}]_3[\text{Re}_4\text{S}_4(\text{CN})_{12}]_2 \cdot 2\text{H}_2\text{O}$ [ORAFET]²⁶⁷ and (right) the corresponding stp underlying net.

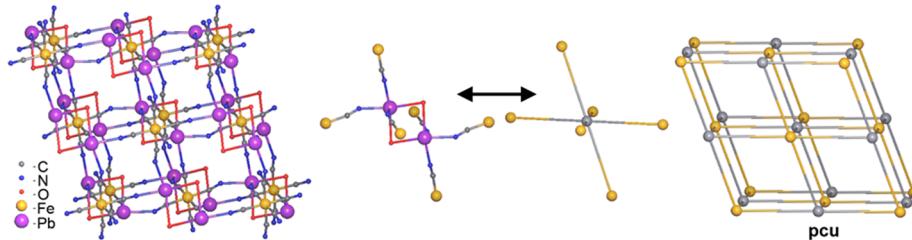


Figure 23. Framework fragment and node (right), coordination figure and underlying net (left) in $\{\text{Pb}(\text{H}_2\text{O})_2\}_2[\text{Fe}(\text{CN})_6]$ [423224].²⁷⁹

5.4.1.3. Complexes with bridging and terminal cyano groups. A striking example of this group are cubane-type cluster anionic cyano complexes $[\text{M}_4\text{Q}_4(\text{CN})_{12}]^{n-}$ ($\text{M} = \text{Mo, W, Re, Q} = \text{S, Se, Te, } n = 3-7$). Unlike cyanometallates with mononuclear nodes, the $\{\text{M}_4\text{Q}_4\}$ core features an unusual number and spatial arrangement of 12 cyano groups; there are no examples though, where all 12 cyano groups are bridging ones. Relatively less studied oxo-centered cubane clusters $[\text{M}_4(\mu_4\text{-O})\text{Te}_4(\text{CN})_{12}]^{6-}$ ($\text{M} = \text{Nb, Ta}$) display the same trend. In $[\text{Ce}(\text{H}_2\text{O})_4(\text{H}_2\text{O})_{2/3}\text{Cl}_{1/3}]_3[\text{Re}_4\text{S}_4(\text{CN})_{12}]_2 \cdot 2\text{H}_2\text{O}$ [ORAFET]²⁶⁷ only six out of 12 cyano groups of the cluster anion are involved in a formation of the 4,6-coordinated stp underlying net with distorted octahedral coordination figures of the nodes (Figure 22).

The steric demand of the terminal ligand also influences the network topology. For example, a combination of *square* and *disphenoidal* coordination figures in a 1:1 ratio occurs in the complexes $[\{\text{ML}\}\{\text{Ni}(\text{CN})_4\}]$ ($\text{M} = \text{Mn, Cd, Zn}; \text{L}$ is a bidentate chelate ligand) with the same square coordination figure of the $[\text{Ni}(\text{CN})_4]^{2-}$ complexes (Table S2). However, in the octahedral mononuclear moieties $\{\text{ML}(\text{NC})_4\}$, terminal chelate ligands L with different steric demand provide a bispheniodal geometry of the node that results in varied framework topologies. For $\text{L} = \text{ethylenediamine}$, a 4,4T3 underlying net occurs in $[\{\text{M}(\text{en})\}\{\text{Ni}(\text{CN})_4\}]$, $\text{M} = \text{Mn, Cd, Zn}$ [CEYGUJ, ENCDNB01, VILXOD].²⁶⁸⁻²⁷⁰ If L is 1,2-propanediamine, a 4,4,4T2 net and a ptt net occur in $[\{\text{Cd}(1,2-pn)\}\{\text{Ni}(\text{CN})_4\}] \cdot 0.5(\text{CH}(\text{Cl}_2)\text{CHCl}_2)$ [JOKYAJ]²⁷¹ and $[\{\text{Cd}(1,2-pn)\}\{\text{Ni}(\text{CN})_4\}] \cdot 0.5(n\text{-C}_5\text{H}_{10})$ [JOKXAI],²⁷¹ respectively. A framework with a 4-coordinated nou underlying topology is realized for $\text{L} = n\text{-methylpropane-1,3-diamine}$ in $[\{\text{Cd}(1,3-pn)\}\{\text{Ni}(\text{CN})_4\}] \cdot 0.5\text{C}_6\text{H}_{12}$ [VEZXED].²⁷²

Bulky terminal ligands can also influence the structure topology by preventing interpenetration. Thus, as opposed to the 2-fold interpenetrating complexes $[\text{MZn}(\text{CN})_4]$ ($\text{M} = \text{Ni, Pd, Pt}$) [169758, 169759, 169760]²⁷³ with a 4-coordinated pts topology, the complexes $[\{\text{ML}_2\}\{\text{Ni}(\text{CN})_4\}]$ ($\text{M} = \text{Cd, Cu, Zn}; \text{L} = \text{pyridine}$) [DULNAA, PANMOH, WAZCAB, ZEZ-GOA]^{265,274-276} with the same topology do not interpenetrate

due to the terminal pyridine ligands filling the framework cavities.

5.4.2. Expansion of nodes. Besides variation of coordination types and ratio between ligands and metal atoms, there are other ways to control the topology of the cyanometallate frameworks. These ways rest upon an expansion of nodes by polynuclear or transition metal cluster complexes. We found such complexes in 218 cyanometallates, whose underlying nets fall into 74 topological types in the cluster representation (see Section 3.1); 6-coordinated pcu (59 compounds) and 4-coordinated dia (20 compounds) topological types predominate. The main relations between the structure of polynuclear complexes and the overall topology of the underlying nets are as follows.

(i) Binuclear complex building units $\{\text{M}_2(\mu\text{-CN})_2\}$ or $\{\text{M}_2(\mu\text{-NC})_2\}$ (Figure 15a) provide the coordination figure of a distorted octahedron, which forms 6-coordinated pcu underlying nets in the $[\text{Cu}_2(\text{CN})_3]$ frameworks. In various combinations with mononuclear complexes, these building units give rise to rare 3,6-coordinated (3,3,3,6T3, 3,6T1, 3,6T28, **pyr, rtl**), 3,4,6-coordinated (3,4,6T32), 4,6-coordinated (4,4,6T65, 4,6T52, 4,6T66, **cai-4,6-Pnma**), or 5,6-coordinated (**btv**) underlying nets, out of which only the 4,6T52 net is found in the cyanometallates with mononuclear nodes (Table S2).

(ii) Other typical binuclear complexes containing water or halogen bridging ligands are $\{\text{M}_2(\mu\text{-X})_2(\text{H}_2\text{O})_2\}$ ($\text{M} = \text{Cd, Mn}; \text{X} = \text{halogen}$) or $\{\text{Pb}_2(\text{H}_2\text{O})_2\}$, which have octahedral coordination figures (Figure 23). They can assemble in a 1:1 ratio with $[\text{Fe}(\text{CN})_6]^{4-}$ [93023, 95566, 423224],²⁷⁷⁻²⁷⁹ $[\text{Os}(\text{CN})_6]^{4-}$ [93025, 95567],^{277,279} $[\text{Ru}(\text{CN})_6]^{4-}$ [93024],²⁷⁷ or the lantern complexes $[\{\text{Cu}_2^+(\text{CN})_2\}(\text{CN})_4]^{4-}$ [XUM-CEO]¹⁷⁶ and in all cases provide a pcu framework topology.

(iii) Polynuclear transition metal clusters strongly influence the overall topology. For 67 cyano complexes with cluster nodes only 21 topological types of underlying nets are realized, and 14 of them are among the most abundant nets found in coordination polymers.⁹⁶ For example, the $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{n-}$ clusters ($\text{Q} = \text{S, Se, Te}, n = 3, 4$) in a 1:1 ratio with Ln^{3+} can provide T-shaped, square, square-pyramidal, or octahedral

coordination figures (Figure 24) depending on the number of terminal ligands. In turn, different Ln^{3+} coordination modes give

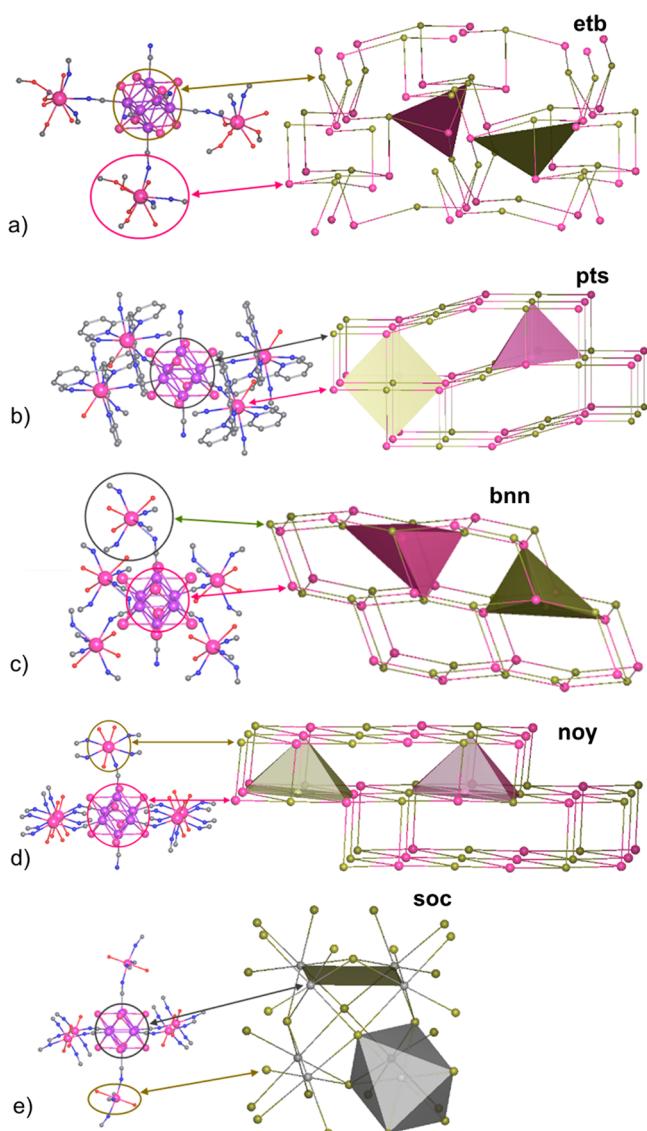


Figure 24. Structure fragments and the corresponding underlying nets in (a) $(\text{H}_3\text{O})\{\text{Nd}(\text{dmf})_3(\text{H}_2\text{O})_3\}\{\text{Re}_6\text{Se}_8(\text{CN})_6\}$ [QUGPAJ],²⁸⁰ (b) $[\text{Nd}(\text{H}_2\text{O})(\text{bipy})_2\{\text{Re}_6\text{Se}_8(\text{CN})_6\}]$ [DIFCEB],²⁸¹ (c) $[\{\text{Gd}(\text{H}_2\text{O})_3\}_2\{\text{Re}_6\text{Te}_8(\text{CN})_6\}\cdot\text{H}_2\text{O}$ [IFEPIT],²⁴¹ (d) $[\text{Ho}(\text{H}_2\text{O})_3]\{\text{Re}_6\text{Se}_8(\text{CN})_6\}\cdot 3.5\text{H}_2\text{O}$,²⁴¹ (e) $(\text{Me}_4\text{N})_2[\text{Co}(\text{H}_2\text{O})_3]\{\text{Re}_6\text{Se}_8(\text{CN})_6\}_2\cdot 4.5\text{H}_2\text{O}$ [IXI-PEK].²⁸³ Nodes (left) and coordination figures (right) are encircled.

rise to a variety of underlying topologies. Thus, in $(\text{H}_3\text{O})\{\text{Nd}(\text{dmf})_3(\text{H}_2\text{O})_3\}\{\text{Re}_6\text{Se}_8(\text{CN})_6\}$ [QUGPAJ],²⁸⁰ an unusual 3-coordinated **etb** framework is composed of *T* shaped and trigonal-pyramidal coordination figures of nodes, while a 4-coordinated **pts** underlying net with square and disphenoidal coordination of nodes occurs in $[\{\text{Nd}(\text{H}_2\text{O})(\text{bipy})_2\}\{\text{Re}_6\text{Se}_8(\text{CN})_6\}]$ [DIFCEB].²⁸¹ In the compounds $[\{\text{Ln}(\text{H}_2\text{O})_3\}\{\text{Re}_6\text{Se}_8(\text{CN})_6\}] \cdot n\text{H}_2\text{O}$ ($n = 3.5$ or 4), 6-coordinated **nia**²⁵⁶ (Figure 18) or 5-coordinated **noy**²⁴¹ underlying nets are realized thanks to trigonal-prismatic 6N(C)+3H₂O or square-antiprismatic 5N(C)+3H₂O coordination of the Ln^{3+} ions, respectively, while, in $[\{\text{Gd}(\text{H}_2\text{O})_3\}_2\{\text{Re}_6\text{Te}_8(\text{CN})_6\}\cdot\text{H}_2\text{O}$ [IFEPIT],²⁴¹ a 5-coordinated **bnn** underlying net emerges. Other examples are the chiral 4-coordinated **uni** framework topology in $(\text{H})[\{\text{M}(\text{H}_2\text{O})_2\}\{\text{Re}_6\text{Se}_8(\text{CN})_6\}]\cdot 2\text{H}_2\text{O}$, $\text{M} = \text{Fe}, \text{Zn}$ [280738],²¹⁷ 3,6-coordinated **pyr** in $[\{\text{Mn}(\text{dmf})_3\}_2\{\text{Re}_6\text{S}_8(\text{CN})_6\}]$ [EFO-SUO],²⁸² 3,6-coordinated rutile-like (**rtl**) in $\text{Na}_2\text{Zn}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2\cdot 23.6\text{H}_2\text{O}$ [280217],²¹⁶ and occasional cases of 6-coordinated **pcu**, 3,6-coordinated 3,3,6T23, and 4-coordinated **sra** underlying nets (Table S2). One of the most spectacular examples of how a polynuclear node can influence the framework topology is the 4,6-coordinated **soc** underlying net in $(\text{Kt})_2[\{\text{M}(\text{H}_2\text{O})_m\}_3\{\text{Re}_6\text{Se}_8(\text{CN})_6\}]_2 \cdot x\text{H}_2\text{O}$ ($\text{Kt}^+ = \text{Cs}^+$, H_3O^+ ; $\text{M}^{2+} = 3d$ metal cation, $m = 1, 2$)^{208,209} (Table S2). This topological type is never realized in mononuclear $[\text{M}(\text{CN})_6]^n$ complexes. It also occurs in $(\text{Me}_4\text{N})_8[\{\text{Mn}(\text{H}_2\text{O})_{1.5}\}_3\{\text{Mo}_6\text{Se}_8(\text{CN})_6\}]_2 \cdot 8\text{H}_2\text{O}$ [KUGFAU], where octahedral molybdenum cyanocluster anion bears a charge of -7 compared to -4 in its rhenium analogue.²⁵⁰ The framework with a higher negative charge of the node is expanded by ~10% to provide space for extra Me_4N^+ cations.

(iv) Additional bridging organic ligands incorporated into the cyanometallate framework extend the nodes, and the corresponding cluster representation is usually described by common nets (**pcu** in 43 compounds, **dia** – 15, **cds** – 8), but their diversity is larger (62 topological types for 151 compounds) in comparison with the cluster cyano complexes or mononuclear cyanides (30 for 105 compounds). Very rare and unusual underlying topologies often appear thanks to such modifying ligands. For example, addition of small amount of 4,4'-bipyridine to the solution of $\text{Cd}(\text{CN})_2$ yields $[\text{Cd}_2(\mu\text{-bipy})(\text{CN})_4]$ [WOFWET],²⁸⁴ where the $\{\text{Cd}_2(\mu\text{-bipy})\}$ dimers are connected via cyano groups into an 8-coordinated 8T7 underlying net. At the same time, the cyanide-bridged subnet of this coordination polymer has a well-known **dia** topology, where each 4,4'-bipyridine molecule fills two adjacent

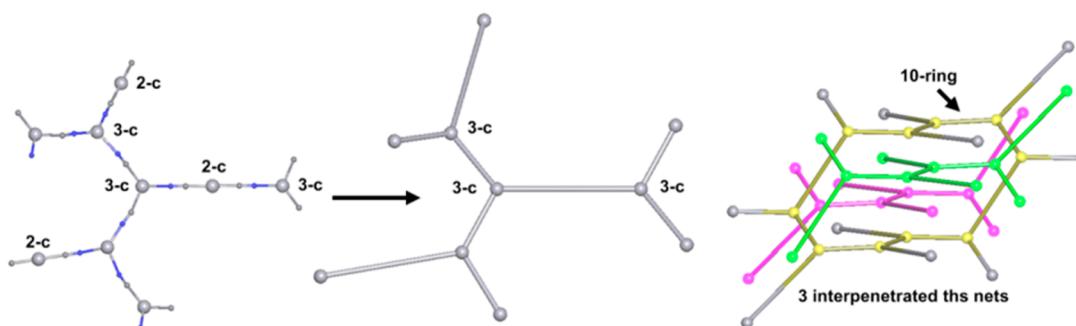


Figure 25. Fragment of the framework in $(\text{Me}_4\text{N})_2[\text{Ag}_6(\text{CN})_8]$ [CEHTEP],²⁸⁸ the corresponding **ths** underlying net, and 3-fold interpenetrating underlying nets, respectively. A ten-membered ring is highlighted in yellow.

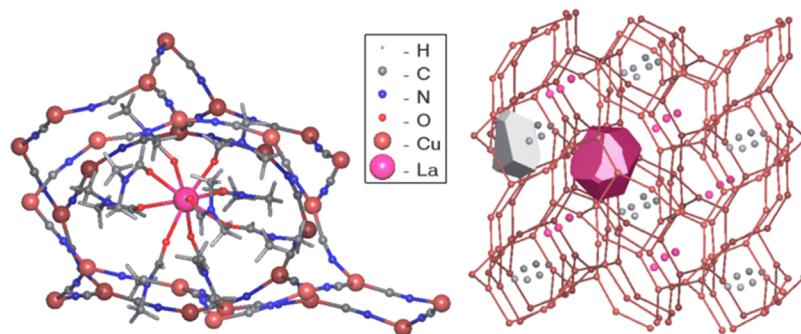


Figure 26. (Left) Extra-framework $[\text{La}(\text{dmf})_9]^{3+}$ cation in the framework cage of $[\text{La}(\text{dmf})_9]_2[\text{Cu}_{12}(\text{CN})_{18}] \cdot 2\text{dmf}$ [FEZCIX]³¹⁴ and (right) positions of the $[\text{La}(\text{dmf})_9]^{3+}$ (magenta balls) and dmf centroids (gray balls) in the corresponding underlying net nos. The Voronoi polyhedra for the two centroids characterize the shape of the cages.

adamantane-like cages. Sometimes such ligands increase free volume and provide interpenetration as it happens, for example, in $[\text{MnAg}_2(\text{bipy})_2(\text{CN})_4]$ [OHUFOM]²⁸⁵ or $[\text{Cu}_6(\text{CN})_6(\mu-\text{L})_3]$ [VAKSUX].²⁸⁶

5.4.3. Extension of edges. Another way to vary the topology of the underlying net is elongation of its edges with enlarged spacers. The following structure correlations can be noted:

(i) Spacer elongation with compact two-coordinated complexes $\{\text{M}(\text{CN})_2\}$ (see Section 4.2.1.3) often leads to interpenetrating frameworks. In total, 56 out of 131 cyano complexes containing elongated spacers include interpenetrating ensembles (Table S2). In this way, long $\{\text{Ag}(\text{CN})_2\}$ and $\{\text{Cu}_2(\mu_2\text{-oxpn})(\text{CN})_2\}$ spacers lead to interpenetration of three **ths** frameworks in $(\text{Me}_4\text{N})_2[\text{Ag}_6(\text{CN})_8]$ [CEHTEP]²⁸⁷ and $[\text{Cu}_4(\text{oxpn})(\text{CN})_4]$ [ARIPUM]. Besides the long spacers, large-membered rings additionally favor interpenetration for low-coordinated networks due to increasing the extra-framework free space (Figure 25).

(ii) For the frameworks containing elongated spacers, the influence of distorting factors decreases, and all cyanometallates of this kind are based on well-known high-symmetric underlying nets, mostly **pcu**, **dia**, **acs**, **cds**, **qtz**, **rob**, **ths**, or **nbo** (Tables S1, S2).

(iii) Bulky spacers of a specific shape as well as voluminous terminal ligands can prevent interpenetration and lead to a framework of a specific rare underlying topology. A convincing example is the series of five cyano complexes $(\text{CoCp}_2)[\text{Fe}\{-\text{Me}_3\text{Sn}(\text{CN})_2\}_3]$ [YUTGEZ],²⁸⁹ $[\text{Co}\{\text{Me}_3\text{M}(\text{CN})_2\}_3]$ ($\text{M} = \text{Pb, Sn}$) [DOMPUQ, KUCXIP],^{290,291} $[\text{M}\{(n\text{-Bu})_3\text{Sn}(\text{CN})_2\}_3]$ ($\text{M} = \text{Co, Fe}$) [TABKIR, TABMAL]. Here the distortion of the octahedral metal coordination leads to a proper change of the framework topology from a high-symmetrical **pcu** (maximum symmetry $Pm\bar{3}m$) to a low-symmetrical **rob** (maximum symmetry $Cccm$), while additional voluminous terminal ligands give rise to another less-symmetrical underlying net **lcy** with the maximum symmetry $P4_132$.

5.4.4. Extra-framework species. Extra-framework species (counterions and/or solvent molecules) modify the geometry of the extra-framework cavities and provide steric restrictions for the framework. Out of the 557 cyano complexes under consideration, the majority (391) contains extra-framework species. Below, the interstitial molecules or ions are sorted by their impact on the framework topology.

(i) Extra-framework metal cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ , Zn^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , or Ni^{2+}) as well as hydroxonium cations slightly distort the cyanometallate framework because

they usually do not form large complexes (cf. group (iv) below). The resulting complexes are mostly based on 6-coordinated **pcu** (42 complexes) or 6-coordinated **nia** (21) underlying nets. In $\text{K}[\text{CuZn}(\text{CN})_4] \cdot 11.2\text{H}_2\text{O}$ [180375],²⁹³ the interstitial hydrated K^+ cations provide a **lon** (lonsdalite) framework topology in contrast to **dia**, which is preferable for the $[\text{M}(\text{CN})_2]^-$ coordination polymers and is realized in 13 complexes (Table S2), including $(\text{Me}_4\text{N})[\text{CuZn}(\text{CN})_4]$ [KEGZOL].⁸² Relatively small extra-framework cations do not prevent the interpenetration; thus, in the $\text{Kt}[\text{M}\{\text{A}(\text{CN})_2\}]$ series ($\text{Kt} = \text{K, Rb}$; $\text{M} = \text{Cd, Co, Mn}$; $\text{A} = \text{Ag, Au}$) [75503, 262503, 281280, 201056]^{108,294-296} a 3-fold interpenetration is observed.

(ii) Inorganic extra-framework anions OH^- , NO_3^- , ClO_4^- , PF_6^- , or $[\text{Cr}(\text{CN})_6]^{3-}$ usually provide a quite common topology: **cds** [WODHED],¹⁰³ **dia** [UJOWIA],²⁹⁷ **pcu** [AMEJOS, AMEJIM, QEQLIY, NOBLOF, NOBLUL, GOB-TEX],^{122,298-300} or **qtz** [IBILUB],³⁰¹ with the only exception of **tcj-4,5-Cmce** [SEHNID, SEHMUO, SEHNEZ].³⁰² It is noteworthy that all the structures with the extra-framework anions are not interpenetrated.

(iii) Expectedly, the influence of organic extra-framework species is more significant. In our sample, we have observed a variety of 22 organic cations and 32 solvate molecules, among which series of homologues or isomers allow tracking the following trends.

Tetramethylammonium and tetraethylammonium cations perfectly fit the cavities in frameworks with **pts** ($(\text{Me}_4\text{N})[\text{CuPt}(\text{CN})_4]$ [JEJFAF])⁸⁴ and **dia** ($(\text{Me}_4\text{N})[\text{MZn}(\text{CN})_4]$, $\text{M} = \text{Cu, Li}$ [KEGZOL, ZITRUP];^{82,303} $(\text{Et}_4\text{N})[\text{LiHg}(\text{CN})_4]$ [DUSTOA1])³⁰⁴ underlying nets. However, further increase of the size of the cation leads to decrease of the framework connectivity: tetrabutylammonium and tetrahexylammonium cations require larger cavities, which exist in 3-coordinated **noe** ($(\text{Bu}_4\text{N})_2[\text{Cu}_4(\text{CN})_6]$ [LUYNAU])³⁰⁵ and 3,3,3,3,3T1 ($(\text{Hex}_4\text{N})_5[\text{Cu}_{10}(\text{CN})_{15}]$ [UJILAA])³⁰⁶ underlying nets. Similarly, change of the extra-framework molecule from methanol to propanol results in reducing the connectivity of the underlying net from a 6-coordinated **pcu** ($[\text{Cu}_2(\text{CN})_3 \cdot \text{MeOH}]$ [260017])³⁰⁷ to a 4-coordinated **nor** ($[\text{Cd}_5(\text{CN})_{10}(\text{H}_2\text{O})_2] \cdot 6\text{PrOH}$ [LATCEO]).³⁰⁸ Even larger solvate molecules do not influence the 4-coordination but alter the topology to **mog** ($[\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{BuOH}$ [KECRAL])³⁰⁹ or **dia** ($[\text{Cd}_5(\text{CN})_{10}(\text{H}_2\text{O})_4] \cdot 4\text{cyh}$ [KUSZED]).³¹⁰

The framework topology also changes in the isomeric series of organic cations or solvate molecules. For example, in the cyano complexes $(\text{Pr}_4\text{N})[\text{Cu}_2(\text{CN})_3]$, 3,6-coordinated **rtl** or **pyr**

topologies appear for di-*n*-propylammonium and di-*i*-propylammonium, respectively. Similarly, propanol ($[Cd_5(CN)_{10}(H_2O)_2] \cdot 6PrOH$ [LATCEO])³⁰⁸ and isopropanol ($[Cd_3(CN)_6(H_2O)_2] \cdot 2(i-PrOH)$ [LATCIS])³⁰⁸ cadmium cyanide clathrates have different 4-coordinated **nor** and **noq** nets.

Organic cations and molecules are large enough to prevent the interpenetration. The node-expanded 2-fold interpenetrated frameworks in $[Cu_2(CN)_2(Me4-pyz)] \cdot dxn$ [ARAWEW],³¹¹ $[Cu_3(CN)_3(dpmp)] \cdot MeCN \cdot H_2O$ [BEPVAV],³¹² and $[Cu_{19}(CN)_{12}(pppt)_6] \cdot 2MeCN$ [PEVBUP] are only three exceptions.³¹³

In some cyano complexes, the framework cavities are occupied by large complex cations that also can decrease the framework connectivity. For example, bulky extra-framework $[Ln(dmf)_9]^{3+}$ cations promote formation of a rare 3-coordinated **nos** underlying net in $[Ln(dmf)_9]_2[Cu_{12}(CN)_{18}] \cdot 2dmf$ ($Ln = La, Eu, Er, Gd$) [FEZCIX, FEZCOD, FEZCUJ, OGOJO]³¹⁴ (Figure 26).

6. CONCLUSIONS

Three-periodic cyanometallates, providing a vast variety of structural types and both chemical and structural diversity of building blocks, proved to be advantageous objects to establish the relations between chemical composition, framework structure, and topological properties of underlying nets.

1. The idealized embeddings of the most preferred topological types (like 4-coordinated **dia** or 6-coordinated **pcu** and **nia**) correspond to the high-symmetry nets possessing coordination figures, rings, and interstitial voids with minimal geometrical distortions, in agreement with Ockwig et al.¹⁰⁵ If the distortions are essential, a rare underlying topology can emerge.

2. The overall topology of an underlying net notably depends on the local environment of the structural fragments (complexing atoms, polynuclear complexes, polydentate ligands) corresponding to the nodes, as well as on the stoichiometry of nodes of different coordination. The shape of the coordination figures significantly restricts possible underlying net topologies (cf. ref 105). For example, the **dia**, **lon**, **lcs**, or **neb** topologies containing tetrahedral coordination figures are improper for the square coordination even if the framework is strongly distorted. Note that the number of possible topologies with specified local topological parameters (coordination number and figure of node, sizes of shortest rings) is much higher than actually found in the crystal structures. Drastic distortion of a coordination figure gives rise to trigonal-pyramidal, disphenoidal, or distorted octahedral environments and, as a result, to rare topologies. A combination of different coordination centers can lead to topologically complicated underlying nets with a hardly predictable topology.

3. In addition to the local topological parameters mentioned above, the following factors can influence the resulting topology of the coordination polymer: (i) terminal ligands with high steric demand, (ii) bulky extra-framework species (solvent molecules, counterions) occupying voids in the three-periodic framework, and (iii) expansion of the coordination center with polynuclear or cluster fragments. They may induce changes in the topology of the resulting three-periodic architecture, particularly providing rings and cavities of different size. Expansion of a mononuclear complex with a cluster anion that bears the same spatial arrangement of cyano groups (for example, $[M_6Q_8(CN)_6]^{n-}$ instead of $[M(CN)_6]^{n-}$) usually preserves the framework topology.

4. Spacer elongation with complexes such as $[Ag(CN)_2]^-$ or $[Au(CN)_2]^-$ usually leads to interpenetrating frameworks. Bulky spacers of a specific shape as well as voluminous terminal ligands can prevent interpenetration and lead to a framework of a rare underlying topology. Furthermore, long flexible (or bent) spacers can somewhat compensate coordination requirements of nodes in favor of the common underlying topologies. However, the interpenetration is still possible if the rings in the underlying net are large enough.

5. The coordination networks in the heteroleptic cyanometallates can be considered as a built up of the cyanide-bridged structural fragments, both finite or polymeric, linked by additional organic spacers. The same topology of the cyanide-bridged fragments occurs in some typical molecular or low-periodic architectures in homoleptic cyanometallates that provide a congener overall topology of the resulting coordination polymer. Here the notion of local environment in the correlation “local topology—overall topology” is extended from finite coordination figure to polymeric low-periodic motif.

Thus, the most frequent topologies **pcu**, **nia**, **dia**, **rtl**, **pts**, **noy**, and *etc.* correspond to statistically the most probable combinations of the aforementioned factors, when the local environment of the nodes fits the most typical (octahedral, tetrahedral, *etc.*) coordination of metal atoms or polyatomic groups with blocked coordination sites taken into account. Moreover, the preferred topologies are essentially resistant to geometrical distortions of structural units. Nevertheless, deviations from the basic topological motif can be to a certain degree controlled, providing wide opportunities for targeted design of cyanometallate crystal structures.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemrev.5b00320](https://doi.org/10.1021/acs.chemrev.5b00320).

Main distributions and topological data on 557 chemically and/or topologically different frameworks in three-periodic cyanometallates as well as on typical cyanide-bridged building blocks in three-periodic cyanometallates with bridging ligands *L*. The data on occurrence of ligands in three-periodic cyanometallates and cyano complexes of different periodicities. ([XLSX](#))

List of abbreviations of molecules and radicals. Notation for connectivity of ligands to metal atoms in coordination compounds. Illustration of the most abundant coordination modes of ligands. Data on coordination polyhedra and coordination figures in the $[M(CN)_8]^{4-}$ ($M = Nb, Mo, W$) cyano complexes. Illustrations of underlying nets for low-periodic cyano complexes, molecular (subgraphs), and polymeric (subnets) cyano structural units (Figures S2–S22). ([PDF](#))

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