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Cyanocomplexes with one-dimensional structures: preparations, crystal structures and magnetic properties

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Contents

Abstract

The review surveys the preparation methods, crystallochemistry and magnetic properties of one-dimensional cyanocomplexes. Their preparation methods are mainly based on reactions in solutions containing suitable building blocks as precursors of the polymeric structure. The analysis of published data on crystal structures is given, as the knowledge of the crystal structure is essential for the study of magneto-structural correlation. Published data on magnetic properties are discussed along with the methods used for the study of magnetic properties. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cyanocomplexes; One-dimensional; Preparation; Crystal structures; Magnetic chains; Spin excitations

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Abbreviations: acacen, *N,N′*-ethylenebis(acetylacetonylideneaminato); 3-ampy, 3-aminopyridine; an, aniline; biquin, 2,2′-biquinoline; bpy, 2,2′-bipyridine; cyclam, 1,4,8,11-tetraazacyclodecane; dien, *N*-(2-aminoethyl)-1,2-ethane-diamine, diethylenetriamine; 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional; DMA, *N,N*-dimethylacetamide; DMF, *N,N′*-dimethylformamide; 3,4-dmpy, 3,4-dimethylpyridine; en, 1,2-diaminoethane; Et, ethyl; hatd, 3,10-bis(7-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane; HB, hydrogen bond; hmtd, *N*-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; iquin, isoquinoline; Me, methyl; mea, 2-aminoethanol; *N*-Meim, *N*-methylimidazolato; 2-MeimH, 2-methylimidazole; 4-Mepy, 4-methylpyridine; Et_4N, tetraethylammonium; Ph, phenyl; pn, 1,2-diaminopropane; tet, triethylenetetraamine; teta, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; thf, tetrahydrofuran; tim, 2,3,9,10-tetramethyl-1,4,8,11-tetrazacyclotetradeca-1,3,8,10-tetraene; tmtu, 1,3-dimethyl-2-thiourea; tpen, *N,N,N′*-tris(2-pyridylmethyl)-*N′*-methyl(ethane-1,2-diamine).

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1. Introduction

Cyanocomplexes were among the first coordination compounds ever prepared, studied, described and used [1–4] and they are still popular in coordination and organometallic chemistry at present. The ability of the cyano group to link various central atoms is used in organometallic and coordination chemistry for the construction of various supercomplexes or molecular assemblies [5–7] and in the field of supramolecular chemistry for building various 1D, 2D or 3D structures [8–14]. The cyanocomplexes exhibiting polymeric structures can mimic the naturally occurring minerals (mineralomimetic structures) [15–18] and form various types of host–guest systems [19–22]. These compounds are interesting as ion exchangers, molecular sieves or materials for storing gases [21]. The attractive properties of the aforementioned compounds can be illustrated by the ability of hexacyano- and pentacyano-nitrosyl complexes to separate gases [23], the use of hexacyanoferrates for silver ion accumulation from dilute solutions [24,25] or radioactive cesium absorption from radioactive waste waters [26]. The use of cyanocomplexes as precursors of homo- and hetero-bimetallic catalysts [27–29], nanosized powders [30] and photosensitizers have also been reported [31]. Cyanocomplexes with a 2D structure can form multilayered thin films on support [32,33].

Recently, cyanocomplexes possessing various degrees of dimensionality and containing paramagnetic central atoms have often been the subject of magnetic studies. In this case, the cyano group or cyanocomplex anion in addition to its structural function also exhibits an important electronic function: it forms an exchange path mediating the interaction among spins localized on paramagnetic centers. Moreover, if the cyanocomplex anion has a non-zero magnetic moment, it also contributes to the magnetic properties of the compound studied, e.g. in the $[Fe(CN)_6]^{3-}$ anion the spin value is $S = 1/2$.

Various physical phenomena associated with magnetism were investigated. Two-dimensional $Fe(py)_2Ni(CN)_4$ complex exhibits 'spin-crossover' behavior [34]. From oligomeric supercomplexes like $Cr\{-CN-Mn(tpen)\}_6(ClO_4)_9 \cdot 3thf$ the high-spin ground states ($S = 27/2$) have been generated [35]. In the 3D $Cr_3^{II}[Cr(CN)_6]_2$ Prussian blue type compound, ferromagnetic (or ferrimagnetic) ordering at a high transition temperature ($T_c = 240$ K) has been achieved [8].

As far as low-dimensional magnetism is concerned, there is a renewed interest in the study of 1D magnets inspired by the latest development in the theory of high-T_c superconductivity [36]. The most popular pairing mechanism in superconductors (e.g. heavy fermion and high-T_c superconductors) is the exchange of antiferromagnetic spin fluctuations. Furthermore, theoretical models developed for these systems are close to those for 1D magnets [37]. Similar analogies exist in using the same theoretical formalism to describe different physical objects, e.g. fractional quantum Hall effect—high-T_c superconductivity—quantum spin chains [38]. Therefore, the uniformity of such a theoretical approach enables better understanding of physical problems in one region by means of solving problems in different regions of physics.

In the last few years the attention of physicists have been focused on the study of spin dynamics in 1D magnetic systems. Their experimental investigations have confirmed a number of theoretically predicted new phenomena that have no parallel in classical and/or 3D physics; the main feature of 1D systems is a failure of the classical spin wave theory which is unable to describe the complexity of the spin dynamics [39]. Recent theoretical studies revealed the importance of quantum fluctuations and non-linear effects in these systems [40]. Consequently, new classes of materials representing quantum spin chains are sought for experimental studies of non-linear magnetic excitations in 1D magnets. It is expected that cyanocomplexes can serve as suitable model compounds for the study of such phenomena.

The main aim of this review is to provide information on the crystallochemistry of 1D cyanocomplexes and their magnetic properties if they have been studied. We will deal neither with cyano bridged oligonuclear complexes (this topic was covered recently by Vahrenkampf et al. [41]) nor the structures and magnetic properties of Prussian blue type compounds, as these were discussed by Verdaguer et al. [42].

In the first part of our paper we will give a short description of the methods used for the preparation of 1D cyanocomplexes. This part is followed by a concise description of binding possibilities of the cyano group. The known structural data on 1D cyanocomplexes, paramagnetic as well as diamagnetic, which are interesting for the sake of comparison, are gathered in Section 4. Important structural data (formula, composition of the cyanocomplex bridging entity(ies), the composition and form of the cationic chromophore) along with references are presented in the form of tables. Each individual table contains structural data on compounds containing a cyanocomplex anion with given coordination number. Within the tables we have classified 1D compounds following the criteria: (i) atomic number of the cyanocomplex central atom; (ii) number of bridging cyano groups; and (iii) atomic number of the cationic central atom. The structural part is followed by a discussion of the magnetic properties of 1D cyanocomplexes.

We hope the information presented will be helpful in understanding the magneto-structural correlation in this class of compounds as well as being stimulating for both chemists and physicists working in the field of 1D materials.

2. Preparation of 1D cyanocomplexes

In general, the synthetic design of a 1D solid can be based upon the so-called 'brick and mortar' method which has already been described for the preparation of 2D and 3D solids [43,44]. The principle of this method is based upon using the assembly of two molecular precursors — building blocks, one of them being the metal central atom coordinated by suitable ligand(s) (brick) and the second being a cyanocomplex anion (mortar). The polymerization of the structure in one direction requires the central atom in the brick to be coordinately unsaturated and to contain vacant coordination sites; alternatively these are formed during the reaction. The first approach to the synthesis can be exemplified by the room temperature preparation of Fe(cyclam)Fe$(CN)_6$ from [Fe(cyclam)]$(ClO_4)_3$ and $K_3[Fe(CN)_6]$ [45]. In the second case, all coordination sites in the precursor of the brick are occupied, but some of them are able to undergo a substitution reaction, in which some of the ligands can be replaced by the nitrogen atoms of the bridging cyano groups, such as occurs during the preparation of $Mn(H_2O)_4Fe(CN)_6 \cdot 4H_2O$. This compound was formed during the reaction of $[Mn(H_2O)_6]Cl_2$ with $(Me_4N)_3[Fe(CN)_6]$ in aqueous solution [11].

The procedures mentioned above sometimes lead directly to single crystals suitable for X-ray analysis, but often one observes product formation in the form of a crystalline precipitate, as in the case of some amine complexes of tetracyanonickelates [46,47]. In this case, the desired single crystals can be obtained by somewhat modified synthetic methods. These are based on the idea of crystallization rate control, which can be achieved by slow inter-diffusion [48] of two precursor solutions, or by the addition of other auxiliary ligand(s) in large excess to the reaction mixture. For this purpose ammonia was used in the preparation of Ni$(bpy)_2$Ni$(CN)_4$; ammonia slowly escapes from the reaction mixture and allows the formation of suitable single crystals of the product [49]. Often an excess of a mixture of 2-aminoethanol and citric acid has been used [50]. These reagents have two effects during the synthesis: they temporarily coordinate the central atom of the brick, and thus avoid the formation of the precipitate, e.g. rapid coordination of bridging cyano groups, and moreover, they control the mother liqueur pH value. This value is important when amines are used as ligands as it may serve for the control of the number of coordinated amine type ligands: at pH > 11 from the aqueous system Cd–en–$Ni(CN)_4^{2-}$ the ionic $[Cd(en)_3][Ni(CN)_4]$ complex crystallizes, at pH ~ 10 two polymorphs of 1D $Cd(en)_2Ni(CN)_4$ form, while lowering the pH below 10 leads to the formation of 3D compound Cd(en)$Ni(CN)_4$ [51].

Cyano groups exhibit polar character and can thus participate in hydrogen bonding (HB). As a consequence, cyanocomplexes are easily soluble in water and the syntheses are mostly carried out in aqueous medium. Addition of methanol, ethanol or acetonitrile to a water solution is sometimes necessary due to the better solubility of the organic ligands used, as in the case of the preparation of Ni$(bpy)_2$Ni$(CN)_4$ [49]. In some cases, the use of non-aqueous solvents such as ethanol [52], DMF or DMA [53] is advantageous for the preparative reactions.

Special conditions are required in the synthesis of air or light sensitive compounds. The synthesis of Eu$(DMF)_4Ni(CN)_4$ was carried out in a dry nitrogen atmosphere due to the presence of the Eu(II) ion [54]. On the other hand, the syntheses of the hexacyanochromates were carried out in darkness [55].

Not fully explored are the procedures based on solid state reactions. In this case a suitable precursor is prepared and the polymerization occurs due to desolvation reaction induced by thermal heating. This method was proposed for the preparation of some new cyanocomplexes by Miyasaki at al. [56]. The disadvantages of this method lie in the fact that it yields only polycrystalline products and, moreover, the control of the solid state reaction is more difficult. Thermal decomposition reactions can also lead to the desired product [57]. Recently, a hydrothermal reaction was used for the preparation of a 1D solid based on copper(I) cyanide [58].

3. Binding modes of the cyano group

The cyano group as a ligand can be bound by various modes. There are two binding modes which are generally the most common and often occur in 1D cyanocomplexes; the cyano group can act as a terminal ligand with the carbon donor atom or the cyano group bonded through both carbon and nitrogen donor atoms acts as a μ_2-bridging ligand [1]. The C-end of the cyano group as a ligand produces a strong field effect, while the N-end of the cyano group behaves as a medium ligand with a ligand field strength lower than ammonia [1]. The carbon–nitrogen distance is usually in the range of 1.12–1.16 Å and no difference was found for the carbon–nitrogen distance whether it is a terminal or bridging ligand. The M–C≡N angle is almost linear or deviates only to a small extent from linearity due to crystal packing forces. On the other hand, the value of the C≡N–M′ angle in the bridging ligand can vary over a wide interval from almost 120 to 180°. An explanation for this observation was suggested by Vahrenkampf [41]; in the M–C(≡N) bond π-bonding plays a significant role, while this is not the case for the M–N(≡C) bond. It can be also assumed that such bent bonds exhibit partially ionic character.

The μ_2-CN group is usually ordered and despite the small difference in the number of electrons on the respective atoms, the present X-ray experiments usually enable one to distinguish between them; as a helping criterion the observed M–C and M–N distances can be used. A disordered cyano group occurs if it links two central atoms of the same kind, e.g. in the –Cu–C≡N–Cu– backbone of the structure of Cu(dien)(CN)Cu$(CN)_2$ [59] or in the $[Ag_2(CN)_3]^-$ anion of Cd(4-Mepy)$_4$Ag$_3$(CN)$_5$ [60].

Among the bonding interactions of the cyano group, HBs can also be included. The cyano group as a terminal ligand can participate in simple or bifurcated HBs of the CN···H – X type (X is an electronegative atom). These HBs may play an important role in packing and stabilizing the structures formed, and sometimes play an important role as a possible exchange path for magnetic interactions [61].

There exist further cyano group binding modes usually observed in organometallic compounds, where it acts as a μ_3-bridging ligand or as a donor of its π-bond electrons [62], but these were not observed in 1D cyanocomplexes and will not be further discussed.

4. Crystallochemistry of 1D cyanocomplexes with different coordination numbers

4.1. General remarks

From the structural point of view, the class of 1D systems contains structures which propagate in one direction of space. Consequently, this definition includes linear or zigzag chains, ladders, ribbons, tubular systems and similar structures. As already mentioned in the previous section, the 'brick and mortar' method [43] can be applied for the construction of 1D systems containing cyanocomplex anion(s) as bridging species. In these materials the appropriate building blocks are linked by μ_2-bridging cyano groups. One can ascribe connectednesses p_1 and p_2 [63], to the brick and to the mortar, respectively. In our case, modifying somewhat the original definition of Wells [63], p is understood as the number of links connecting the given block to its neighbor blocks within the 1D system. The 1D system of the p_1,p_2 type with alternating blocks can be formed, if both p_1 and p_2 are equal to or higher than 2. The simple chain with alternating blocks depicted as

–A–B–A–B–A–B–

can be coded as a 2,2 chain. In this scheme the letter A represents the cationic block (brick) and the letter B represents the cyanocomplex anion (mortar).

The notation using the numbers p_1 and p_2 can be extended for some types of coordination polyhedra, e.g. octahedron, by the symbols *T* (*trans*), *C* (*cis*), *F* (*fac*) or *M* (*mer*) to express the positions of the bridging cyano groups on the central atom of the block. Thus a 2,2-*TT* chain (see Scheme 1(a)) is a symbol of the 1D structure with two bridging cyano groups in the cation as well as in the anion and both are in *trans* positions in the respective coordination polyhedra.

Occasionally, a 1D system can be created only by the linkage of cyanocomplex anions. This behavior is characteristic for some cyanocuprates, in which Cu(I) atoms are linked by bridging cyano groups in the form –Cu–Cu–Cu–, while the cations are linked as terminal groups to the copper atoms or bound in the structure only by ionic bonds (Scheme 1(k)). In this type of structure no alternation of the building blocks occur and consequently the connectedness of the cationic block can be 1 or even 0. We have included these compounds in Table 1 as the propagation of the structure is achieved via cyanocomplex anions.

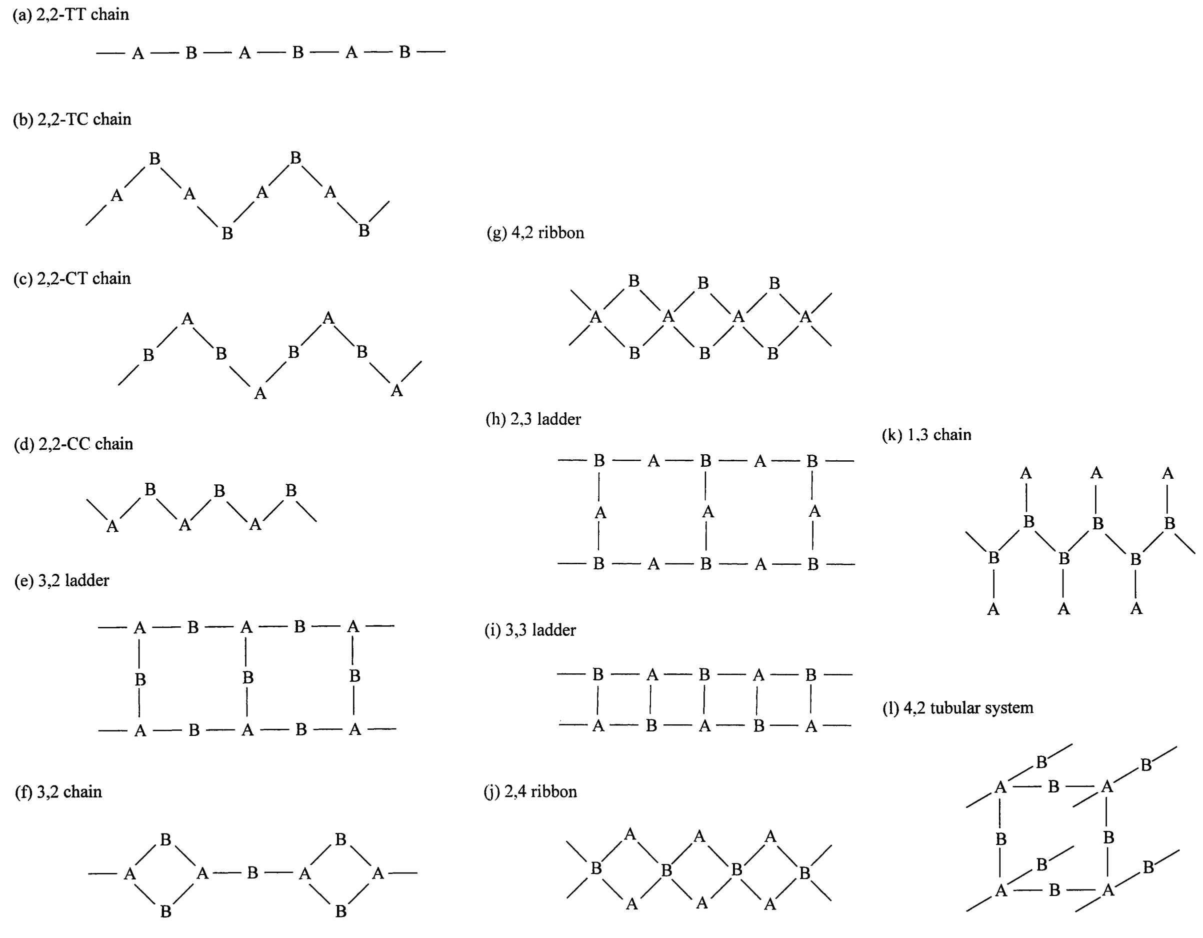
The 1D system formed can be electroneutral or electrically charged. In the latter situation the sign and net charge on the 1D backbone depends on the charges and number of building blocks used in its formation. The resulting charge is counterbalanced by suitable cation(s) or anion(s), respectively, such as $[Ph_4P]^+$ in $[Ph_4P][Ni(pn)_2Fe(CN)_6]\cdot H_2O$ [64] or $[Ag(CN)_2]^-$ in Cu(en)$_2$Ag$_2$(CN)$_4$ [65]. The highest value of the charge (+6) per 'monomeric' unit was observed in $[(DMF)_{16}Yb_6O(OH)_8Pd(CN)_4][Pd(CN)_4]_3\cdot 4DMF$ [66].

Some possible 1D systems are depicted in Scheme 1. This scheme includes chain-, ribbon- or ladder-like systems with maximal p equal to 4 and cannot be considered as exhaustive. Most of the systems (a)–(k) have been observed as real structures. One can also foresee the formation of tubular 1D systems with connectedness 4,2 (Scheme 1(l)), but to our knowledge such systems have not been realized yet.

4.2. Coordination number 2

Coordination number 2 is characteristic for the silver atom in the $Ag(CN)_2^-$ anion. Linear coordination was sometimes also found for Cu(I) atoms, e.g. in polymeric Cu(NH$_3$)$_2$Cu$_4$(CN)$_6$ [67]. The formation of a 1D structural motif requires both cyano groups in the dicyanoargentate anion to exhibit bridging character. If the charge of the cation in dicyanoargentates is higher than +1, the chains formed are positively charged. As can be seen from Table 1, seven chain-like compounds containing bridging dicyanoargentate anions have been structurally characterized to date, and among them only three contain a paramagnetic central atom, namely Cu(II).

The structure of Cu(en)$_2$Ag$_2$(CN)$_4$ [65] is built up of infinite positively charged $[\text{–NC–Ag–CN–Cu(en)}_2\text{–}]_n^{n+}$ chains with a tetragonally deformed octahedral coordi-



(a) 2,2-TT chain

(b) 2,2-TC chain

(c) 2,2-CT chain

(d) 2,2-CC chain

(e) 3,2 ladder

(f) 3,2 chain

(g) 4,2 ribbon

(h) 2,3 ladder

(i) 3,3 ladder

(j) 2,4 ribbon

(k) 1,3 chain

(l) 4,2 tubular system

Scheme 1. Possible types of 1D systems.

nation sphere of the copper atom (Fig. 1). The positive charge of the chain is counterbalanced by free Ag(CN)$_2^-$ anions. Such linear 2,2-*TT* chains were also found in several diamagnetic compounds containing Cd(II) atoms (Table 1). We can mention the 2,2-*TT* chain-like structure of Cd(3-ampy)$_3$Ag$_2$(CN)$_4$ as an interesting example; the chain formed is electroneutral, because the second dicyanoargentate anion is coordinated as a terminal ligand to the Cd atom [68].

In the Cu(bpy)$_2$Ag$_2$(CN)$_4$ · H$_2$O the bulky bpy ligands cannot occupy the positions in the equatorial plane around the central atom, they are twisted away and the bridging cyano groups are bound in *cis* positions. The crystal structure is completed by free Ag(CN)$_2^-$ anions and water molecules of crystallization [69]. Similar bent chains are present in the structure of {Cu$_2$(dien)}$_2$-Ag$_5$(CN)$_9$ which contain Ag$_2$(CN)$_3^-$ anion as counterion [70]. This anion is formally formed by condensation of two Ag(CN)$_2^-$ anions. The same binuclear anion links Cd central atoms within the chain found in diamagnetic [Cd(4-Mepy)$_4$Ag$_2$(CN)$_3$)][Ag(CN)$_2$] (Fig. 2) [60] yielding longer spacing between cationic central atoms.

4.3. Coordination number 3

The trigonal coordination of a central atom by cyano groups is a relatively rare case. It was reported almost exclusively for Cu(I) in the form of the free Cu(CN)$_3^{2-}$ anion [71], or as a trigonally coordinated copper atom forming part of a polymeric structure [67].

To our knowledge, no 1D structure built up of [–NC–Cu(CN)–CN–ML$_n$–] type chains has been described. For cyanocuprates the polymerization of the anion itself and the formation of the [–Cu(CN)–CN–]$_n^{n-}$ type chains is characteristic. The

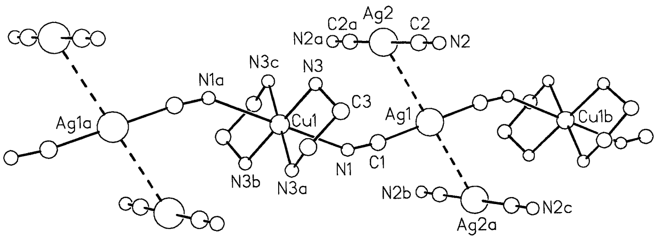


Fig. 1. Crystal structure of Cu(en)$_2$Ag$_2$(CN)$_4$ [65]. Hydrogen atoms are omitted. Argentophilic interactions are displayed by dashed lines.

Table 1
1D structures containing cyanocomplex anions with coordination numbers 2 and 3

Formula and 1D type	Bridging unit	Chromophore of the cation	Reference
$Cu(en)_2Ag_2(CN)_4$ 2,2-*TT* chain	–NC–Ag–CN–	*trans*-CuN_4N_2 Tetragonal bipyramid	[65]
$\{Cu(dien)\}_2Ag_5(CN)_9$ 2,2-*CT* chain	–NC–Ag–CN–	*cis*-CuN_3N_2 Square pyramid	[70]
$Cu(bpy)_2Ag_2(CN)_4 \cdot H_2O$ 2,2-*CT* chain	–NC–Ag–CN–	*cis*-CuN_4N_2 Octahedron	[69]
$Zn(en)_2Ag_2(CN)_4$ 2,2-*TT* chain	–NC–Ag–CN–	*trans*-ZnN_4N_2 Octahedron	[104]
$Cd(4\text{-}Mepy)_4Ag_3(CN)_5$ 2,2-*TT* chain	–NC–Ag–C,N–Ag–CN–	*trans*-CdN_4N_2 Octahedron	[60]
$Cd(N\text{-}Meim)_4Ag_2(CN)_4$ 2,2-*TT* chain	–NC–Ag–CN–	*trans*-CdN_4N_2 Octahedron	[50]
$Cd(2\text{-}MeimH)_4Ag_2(CN)_4 \cdot H_2O$ 2,2-*TT* chain	–NC–Ag–CN–	*trans*-CdN_4N_2 Octahedron	[50]
$Cd(3\text{-}ampy)_3Ag_2(CN)_4$ 2,2-*TT* chain	–NC–Ag–CN–	*trans*-CdN_3NN_2 Octahedron	[68]
$Cd(3,4\text{-}dmpy)_4Ag_3(CN)_5$ 2,2-*TT* chain	–NC–Ag–CN–Ag–CN–	*trans*-CdN_4N_2 Octahedron	[68]
$Cu(dien)(CN)Cu(CN)_2$ 1,3 Chain	–Cu–C,N–	$CuCN_3N$ Square pyramid	[59]
$Cu(NH_3)_3Cu_2(CN)_4$ 2,3 Ribbon, see text	$–Cu_2(–CN–)(–C,N–)_3$	CuN_3NN_2 Octahedron	[78]
$Zn(NH_3)_3Cu_2(CN)_4$ 1,2 Chain, see text	–Cu–C,N–	ZnN_3N Tetrahedron	[72]
$Cu(biquin)Cu_3(CN)_4$ 1,3 Chain	$–Cu–(C,N–Cu–C,N)_2–$	$Cu(C,N)N_2$ Trigonal	[58]

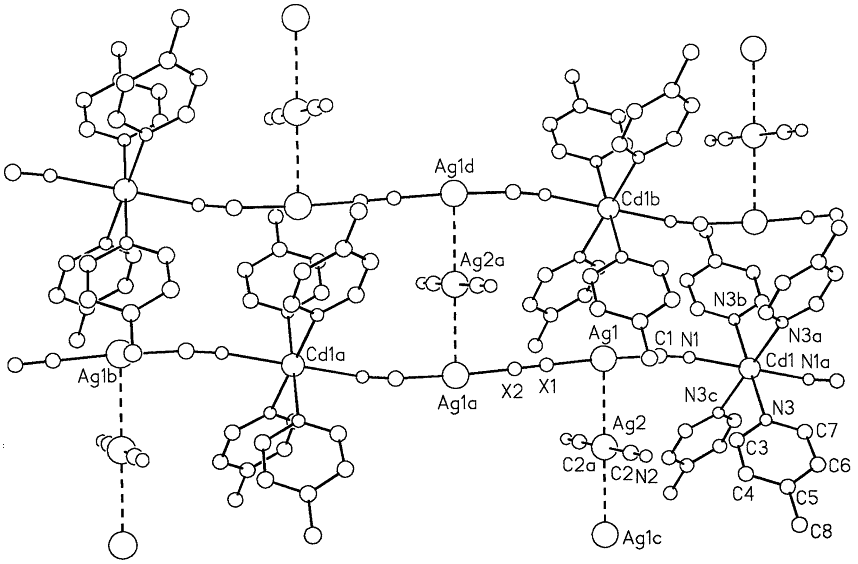


Fig. 2. Linear 2,2-TT structure of $[Cd(4\text{-}Mepy)_4Ag_2(CN)_3)][Ag(CN)_2]$ with $[Ag_2(CN)_3]^-$ bridging unit [60]]. Hydrogen atoms are omitted. Argentophilic interactions are displayed by dashed lines. X1 and X2 are atoms of the disordered cyano group.

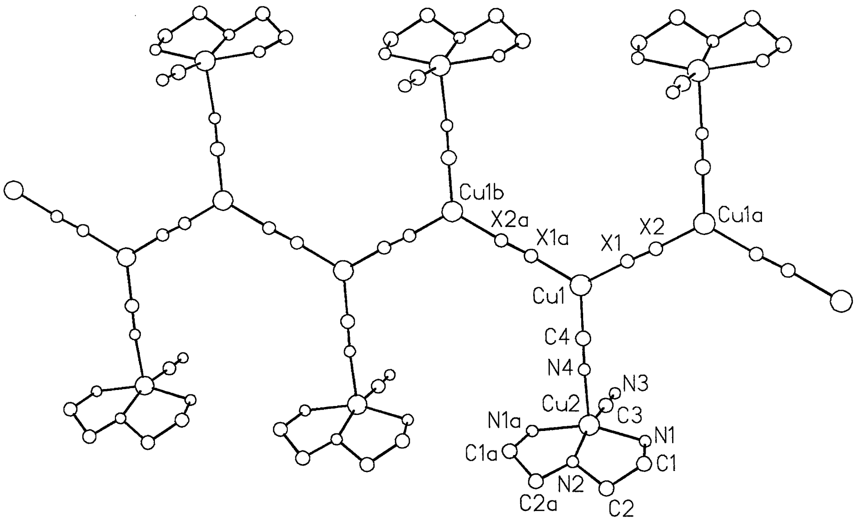


Fig. 3. 1D structure of $Cu(dien)(CN)Cu(CN)_2$ [59]. Hydrogen atoms are omitted. X1 and X2 are atoms of the disordered cyano group.

cyano groups within these chains are often disordered. The negative charge of the chains is counterbalanced by the charge of appropriate cations bound to cyano groups not involved in the chain propagation. This type of structure was found in the paramagnetic complex $Cu(dien)(CN)Cu(CN)_2$ [59] (Fig. 3) and in diamagnetic ones $Zn(NH_3)_3Cu_2(CN)_4$ [72] and $Cu(biquin)Cu_3(CN)_4$ [58]. In the first compound the $[Cu(dien)(CN)]^+$ cations with square pyramidal coordinated copper atoms are bound to each 'free' cyano group, while in the second case the $[Zn(NH_3)_3]^{2+}$ cations containing tetrahedrally coordinated zinc atoms are bound to every second 'free' cyano group. The third compound exhibits a more complicated $[Cu_3(CN)_4]^-$ backbone formed of two-coordinate $Cu(CN)_2$ and three-coordinate $Cu(CN)_3$ sites. Such chains were also reported in some alkali cyanocuprates, e.g. in $KCu(CN)_2$ [73] or $NaCu(CN)_2 \cdot 2H_2O$ [71], and similar chains are typical for some adducts of copper cyanide like $CuCN \cdot NEt_3$ [74,75] and two polymorphs of CuCN · tmtu [76]. Three-coordinate Cu(I) atoms are present in some 1D materials formed from the CuCN–tiazolate–organoamine systems [77].

The trigonal coordination of Cu(I) atoms is preserved in the 2,3 ribbon-like 1D structure observed in $Cu(NH_3)_3Cu_2(CN)_4$ [78]. In this compound four Cu(I) atoms and one Cu(II) atom form irregular pentagons, which share opposite edges along the ribbon direction. The Cu(II) atoms are hexa-coordinated; two sites are occupied by bridging cyano groups and three ammonia ligands statistically occupy the remaining four coordination sites.

4.4. Coordination number 4

Two different geometries are possible for tetra coordination: tetrahedral and square planar. Cyanocomplexes with both types of geometry are known. Although there is a large number of cyanocomplexes exhibiting tetrahedral coordination of the central atom in the anion, these are mostly 3D from the crystallochemical point of view. We can mention as examples cyanocadmates(II) [22,79,80]. Surprisingly, to our knowledge, no 1D structure containing a cyanocomplex anion with tetrahedral symmetry was reported. We believe such compounds may exist but at present we are not aware of any effort devoted to the preparation of such a compound.

Square coordination is characteristic for Ni(II), Pd(II) and Pt(II). Among these, tetracyanonickelates are the most widely studied, especially with regard to their ability to form different types of inclusion compounds [19]. Twenty-five compounds with square cyanocomplex anions exhibiting 1D structures are collected in Table 2.

One, two, three or four cyano groups in the $[M(CN)_4]^{2-}$ anion can exhibit bridging character; all four possibilities have been found. The bridging character of only one cyano group does not enable the propagation of the structure, only oligomeric structures, as in recently reported binuclear $Cu(dien)(mea)Ni(CN)_4 \cdot 2H_2O$ [81], are formed. All other possibilities allow formation of 1D structures. The analysis of possible 1D structure types from a geometrical point of view has already been given by Iwamoto [19].

The bridging character of two cyano groups results in linear 2,2-TT or 2,2 zigzag-like chains of CT, TC or CC types. The 2,2-TT type of chain is rather common (see Table 2), and for the first time it was found in $Ni(en)_2Pd(CN)_4$ (Fig. 4) [82]. The important feature of this compound is that the $Ni(en)_2(NC)_2$ octahedron is compressed along the chain direction. The opposite was observed in the isostructural $Ni(en)_2Ni(CN)_4$ [83]. The 2,2-CT type of chain is formed by a magnetically interesting $Ni(bpy)_2Ni(CN)_4$ compound; the bulky bpy

Table 2
One-dimensional structures containing cyanocomplex anions with coordination number 4

Formula and 1D type	Bridging unit	Chromophore of the cation	Reference
$Ni(en)_2Ni(CN)_4$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-NiN_4N_2 Octahedron	[83]
$Ni(en)_2Ni(CN)_4 \cdot 2.16H_2O$ 2,2-*CCTC* chain	*cis* $-NC-Ni(CN)_2-CN-(2\times)$	*trans*-NiN_4N_2 Octahedron *cis*-NiN_4N_2 Octahedron	[84]
$Ni(en)_2Ni(CN)_4 \cdot 2an$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-NiN_4N_2 Octahedron	[105]
$Ni(pn)_2Ni(CN)_4 \cdot H_2O$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-NiN_4N_2 Octahedron	[46]
$Ni(bpy)_2Ni(CN)_4$ 2,2-*CT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*cis*-NiN_4N_2 Octahedron	[49]
$Ni(tim)Ni(CN)_4$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-NiN_4N_2 Octahedron	[106]
$Ni(hmtd)Ni(CN)_4 \cdot H_2O$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-NiN_4N_2 Elongated tetragonal bipyramid	[107]
$Cu(en)_2Ni(CN)_4$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-CuN_4N_2 Elongated tetragonal bipyramid	[108]
$Cu(en)_2Ni(CN)_4 \cdot 2an$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-CuN_4N_2 Elongated tetragonal bipyramid	[105]
$Zn(en)_2Ni(CN)_4$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-ZnN_4N_2 Octahedron	[109]
$Zn(en)_2Ni(CN)_4 \cdot 2an$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-ZnN_4N_2 Octahedron	[105]
$Cd(en)_2Ni(CN)_4$ (monoclinic) 2,2-*CC* chain	*cis* $-NC-Ni(CN)_2-CN-$	*cis*-CdN_4N_2 Octahedron	[51]
$Cd(en)_2Ni(CN)_4$ (orthorhombic) 2,2-*CC* chain	*cis* $-NC-Ni(CN)_2-CN-$	*cis*-CdN_4N_2 Octahedron	[51]
$Cd(en)_2Ni(CN)_4 \cdot 2an$ 2,2-*TT* chain	*trans* $-NC-Ni(CN)_2-CN-$	*trans*-CdN_4N_2 Octahedron	[105]
$(DMF)_5Sm[Ni(CN)_4]Cl$ 2,2 Chain	*trans* $-NC-Ni(CN)_2-CN-$	SmN_2O_5Cl Square antiprism	[53]
$(DMF)_4EuNi(CN)_4$ 3,3 Ladder	$-NC-Ni(CN)(-CN-)_2$	EuN_3O_4 Capped trigonal prism	[54]
$(DMF)_{10}Er_2[Ni(CN)_4]_3$ 3,2 Chain	*trans* $-NC-Ni(CN)_2-CN-$ *cis* $-NC-Ni(CN)_2-CN-$	ErN_3O_5 Square antiprism	[53]
$(DMF)_5Yb[Ni(CN)_4]Cl$ 2,2 Chain	*trans* $-NC-Ni(CN)_2-CN-$	YbN_2O_5Cl Pentagonal bipyramid	[53]
$(DMF)_{10}Yb_2[Ni(CN)_4]_3$ 3,2 Chain	*trans* $-NC-Ni(CN)_2-CN-$ *cis* $-NC-Ni(CN)_2-CN-$	YbN_3O_5 Square antiprism	[12]
$Ni(en)_2Pd(CN)_4$ 2,2-*TT* chain	*trans* $-NC-Pd(CN)_2-CN-$	*trans*-NiN_4N_2 Octahedron	[82]
$Cu(en)_2Pd(CN)_4$ 2,2-*TT* chain	*trans* $-NC-Pd(CN)_2-CN-$	*trans*-CuN_4N_2 Elongated tetragonal bipyramid	[110]
$(DMF)_{10}Yb_2[Pd(CN)_4]_3$ 3,2 Ladder	*trans* $-NC-Ni(CN)_2-CN-$ *cis* $-NC-Ni(CN)_2-CN-$	YbN_3O_5 Square antiprism	[53]
$[(DMF)_{16}Yb_6O(OH)_8$ $Pd(CN)_4][Pd(CN)_4]_3 \cdot 4DMF$ 2,2-*TT* chain	*trans* $-NC-Pd(CN)_2-CN-$	$Yb(III)NOO_2O_4$ In cluster $Yb_6OO_8O_{16}$ Square antiprism	[66]
$(DMF)_4EuPt(CN)_4$ 3,3 Ladder	$-NC-Pt(CN)(-CN-)_2$	EuN_3O_4 Capped trigonal prism	[54]
$(DMF)_{10}Yb_2[Pt(CN)_4]_3$ 3,2 Ladder	*trans* $-NC-Ni(CN)_2-CN-$ *cis* $-NC-Ni(CN)_2-CN-$	YbN_3O_5 Square antiprism	[12]

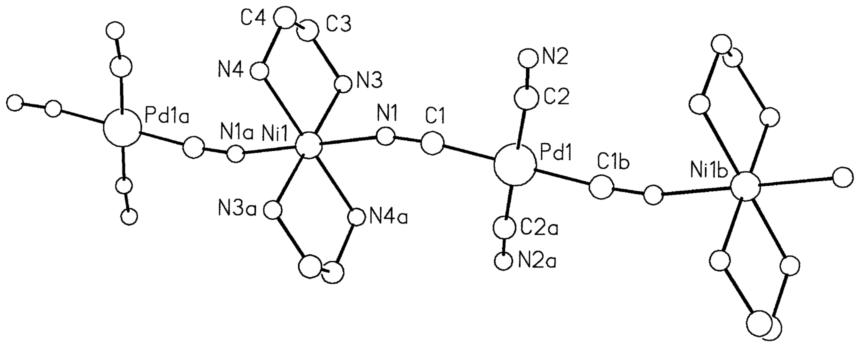


Fig. 4. 2,2-TT chain in the structure of $Ni(en)_2Pd(CN)_4$ [82]. Hydrogen atoms are omitted.

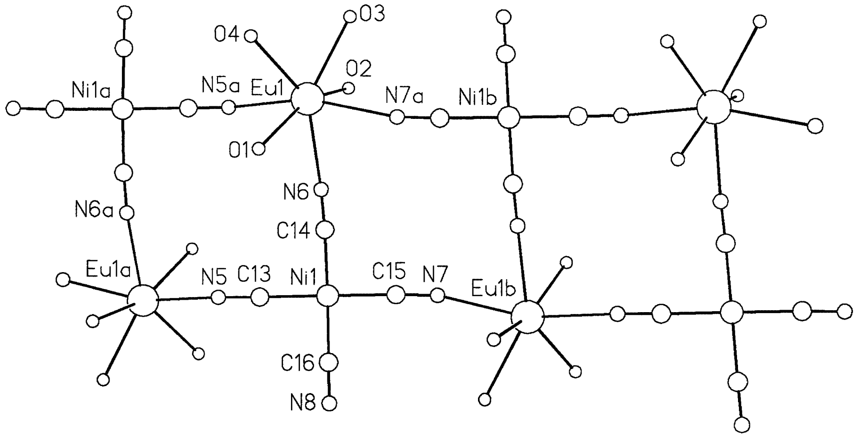


Fig. 5. 3,3 Ladder-like structure formed by $(DMF)_4EuNi(CN)_4$ [54]. Only the O donor atoms of the DMF ligands are shown for the sake of clarity.

ligands forced the *cis* coordination of bridging cyano groups [49]. A 2,2-CC type of chain was found in two polymorphs of diamagnetic $Cd(en)_2Ni(CN)_4$. Their structures differ only by relative positions of neighboring chains [51]. On the other hand, a 2,2-TC type of chain has not been described yet.

Mixed types of chains with higher periodicity may also be formed. A higher periodicity of the repeating motif of the chain, namely the CCTC type, was found in the structure of $Ni(en)_2Ni(CN)_4 \cdot 2.16H_2O$; in this compound all the bridging cyano groups are placed in *cis* positions in the anions, while *cis* and *trans* arrangements of the bridging cyano groups alternate in the cations [84].

As suggested in Section 4.1, different types of ladder-like structures using square anions may be formed. As an example the 3,3 ladder structure type (Scheme 1(i)) has been seen in the structures of $(DMF)_4EuM(CN)_4$ (M = Ni, Pt) (Fig. 5) [54]. In this ladder-like structure Ni(II) (or Pt(II)) and Eu(II) atoms joined by bridging cyano groups alternatively repeat. The fourth cyano group is terminal. Hepta coordination of the Eu(II) atoms is formed by three nitrogen atoms of the bridging cyano groups and four oxygen atoms from DMF molecules. This type of ladder is not a real spin ladder as the nickel atom is diamagnetic. Two crystallographically different square anion with *cis* and *trans* positions of the bridging cyano groups were found in $(DMF)_{10}M_2[Ni(CN)_4]_3$ (M = Er, Yb) [53]. These compounds are of the *f* structure type (Scheme 1).

Geometrical considerations suggest the possibility of 1D structure formation of the 2,4 ribbon shape with double cationic bridge (see Scheme 1(j)), in which all four cyano groups exhibit a bridging function; such structures have not been found yet among square tetracyanocomplexes.

4.5. Coordination number 5

Penta coordinated cyanocomplex anions are scarce. Their existence was reported in ionic pentacyanonickelates(3 −) containing both trigonal bipyramidal as well as square pyramidal $[Ni(CN)_5]^{3-}$ anions [85]. To our knowledge, no 1D structure containing a $[M(CN)_5]^{x-}$ type cyanocomplex anion has yet been found. On the other hand, a diamagnetic $[Cd(iquin)_2][Cd(CN)_3(iquin)_2]_2$ 1D compound was described with a 4,2 ribbon-like structure (Scheme 1(g)). In this compound the cation is octahedrally coordinated by four bridging N-bonded cyano groups in the equatorial plane and two iquin molecules in the axial positions; the anion is penta coordinated in the trigonal bipyramidal form, but it contains only three cyano groups, two among them bridging. The axial positions are occupied by iquin molecules [86], so it is not a really penta coordinated cyanocomplex and therefore we have not included it in our tables. Stereochemical considerations suggest the possibility of formation of various 1D structures; they could exhibit different shapes depending on the symmetry (D_{3h} or C_{4v}) of the anion and on the positions of bridging cyano ligands in the coordination spheres of the anion as well as cation.

4.6. Coordination number 6

Hexa coordinated cyanocomplexes are common. Such anions form a large variety of compounds prevailingly with ionic or 3D structure [42,87]. On the contrary, there are not as many hexa coordinated anions with 1D structures at present. Seventeen examples of the latter type of compounds are known and they are gathered in Table 3; some of them form isostructural series. We have also included in this table $Ni(en)_2Fe(CN)_5(NO)\cdot H_2O$ [88] due to the similarity of the nitroprusside anion with the corresponding cyanocomplex anion.

Perfectly linear negatively charged chains of 2,2-TT type were found in $[Me_4N][Mn(H_2O)_4M(CN)_6]\cdot 4H_2O$ (M = Mn(III), Fe(III)) [11]. In both structures two cyano groups placed in the *trans* positions in the anion are used to link Mn(II) and M(III) atoms. The coordination polyhedron of Mn(II) is completed by four water molecules placed in the equatorial plane. Water molecules of crystallization occupy sites between the chains; they interact with one another and with the terminal cyano groups from the chains via HBs.

Chains of TC type form part of the structures of $[Ph_4P][Ni(pn)_2M(CN)_6]\cdot H_2O$ [M = Cr(III), Fe(III), Co(III)]. The zigzag chain is negatively charged, so the electric balance is achieved by the presence of bulky tetraphenylphosphonium cations [55].

A 2,4 ribbon type 1D structure (double bridged chain), which has not been observed among the tetracyanocomplexes, forms a part of the recently published structure of the $[Cu(dien)]_3[Fe(CN)_6]_2\cdot 6H_2O$ (Fig. 6) [48]. This compound can be reformulated as $[Cu_2(dien)_2Fe(CN)_6]n\cdot n[Cu(dien)(H_2O)Fe(CN)_6]\cdot 5n$-$H_2O$. It consists of infinite positively charged ribbons formed by joining vertices (Fe(III) atoms) of squares. The squares are built up from two Cu(II) and two Fe(III) atoms linked by bridging cyano groups (four of six in the anion). The coordination of the copper atom is completed to five by one chelate bonded dien molecule. The positive charge of the ribbon is counterbalanced by negatively charged dimeric anions. The same structures exhibit isomorphous hexacyanocobaltate(III) and hexacyanochromate(III) compounds [89,90].

Deformed 2,3 ladder-like structures were reported for $[Ni(en)_2]_3[M(CN)_6]_2\cdot 3H_2O$ (M = Fe(III) or Co(III) [91]. Two different $[Ni(en)_2]^{2+}$ cations are present in these compounds; in the first one the bridging cyano groups are in *trans* positions and in the second one in *cis* positions of the deformed octahedra. These cations are linked through a $M(CN)_6$ bridging entity in which the bridging cyano groups occupy the *mer* positions (Fig. 7).

Geometrical considerations suggest the possibility of the formation of some other types of 1D structures. All these types would require halting the polymerization process of the structure at the first step in two directions.

4.7. Coordination numbers 7 and higher

Elements of the second and third transition series, e.g. Mo, W, etc. often form cyanocomplexes with coordination numbers higher than 6 (Table 4). Only one example of a 1D structure with such a high coordination number has been published very recently: $Ni_2(NH_3)_9Mo(CN)_8\cdot 2H_2O$. Its structure is formed of 2,2 chains in which *cis*-$Ni(NH_3)_4N_2$ octahedra and –NC–Mo-$(CN)_6$–CN– dodecahedra are linked. The electroneutrality of the chain is achieved by terminal linking of the $[Ni(NH_3)_5]^{2+}$ cations to each cyanocomplex anion [92].

5. Magnetic properties of 1D cyanocomplexes

In the beginning of this section the motivation of physicists to study the magnetic properties of quantum spin chains is formulated. It was especially the divers spin dynamics of magnetic chains which stimulated theoretical and experimental interest in this class of materials. In most 3D magnets at temperatures much lower than the temperature of magnetic ordering the concept of spin waves as the small spin deviations from the ordered ground state can be applied for satisfactory interpretation of the experimental data. On the other hand, 1D magnets are characterized by strong spin fluctuations which prevent the onset of magnetic ordering at any non-zero temperature and give rise to other kinds of spin excitations significantly different from spin waves. It has been showed that the nature of the ground state and magnetic excitations depends on the spin value, ratio of the exchange coupling constant and parameters describing anisotropy induced by crystal field as well as the magnitude and orientation of the external magnetic field [93,94].

Experimental techniques used for studies of magnetic properties of 1D magnets usually involve specific heat, magnetization and susceptibility measurements for determination of the sign and magnitude of the exchange

Table 3
Cyanocomplexes with hexa coordinated central atom exhibiting 1D structures

Formula and 1D type	Bridging unit	Chromophore of the cation	Reference
[Ph$_4$P]Ni(pn)$_2$Cr(CN)$_6$ · H$_2$O 2,2-*TC* chain	*cis* –NC–Cr(III)(CN)$_4$–CN–	*trans*-NiN$_4$N$_2$ octahedron	[55]
[Cu$_2$(dien)$_2$Cr(CN)$_6$]$_n$ *n*[Cu(dien)(H$_2$O)Cr(CN)$_6$] · 5*n*H$_2$O 2,4-Ribbon	*trans* (–NC–)$_2$Cr(III)(CN)$_2$(–CN–)$_2$ –NC–Cr(III)(CN)$_5$	*cis*-CuN$_3$N$_2$ (2 ×) CuN$_3$NO Square pyramid	[90]
[Me$_4$N]MnMn(CN)$_6$ · 8H$_2$O 2,2-*TT* chain	*trans* –NC–Fe(III)(CN)$_4$–CN–	*trans*-Mn(II)O$_4$N$_2$ Octahedron	[11]
[Me$_4$N]MnFe(CN)$_6$ · 8H$_2$O 2,2-*TT* chain	*trans* –NC–Fe(CN)$_4$–CN–	*trans*-Mn(II)O$_4$N$_2$ Octahedron	[11]
[Et$_4$N]$_2$Mn(acacen)Fe(CN)$_6$ 2,2-*TT* chain	*trans* –NC–Fe(III)(CN)$_4$–CN–	*cis*-Mn(III)O$_2$N$_2$N$_2$ Octahedron	[52]
Fe(cyclam)Fe(CN)$_6$ 2,2-*TT* chain	*trans* –NC–Fe(CN)$_4$–CN–	*trans*-FeN$_4$N$_2$ Octahedron	[45]
[Ph$_4$P]Ni(pn)$_2$Fe(CN)$_6$ · H$_2$O 2,2-*TC* chain	*cis* –NC–Fe(III)(CN)$_4$–CN–	*trans*-NiN$_4$N$_2$ Octahedron	[64]
[Ni(en)$_2$]$_3$[Fe(CN)$_6$]$_2$ · 3H$_2$O 3,2 Ladder	*mer* –NC–Fe(III)(CN)$_3$(–CN–)$_2$	*cis*-NiN$_4$N$_2$ Octahedron *trans*-NiN$_4$N$_2$ Octahedron	[91]
Ni(en)$_2$Fe(CN)$_5$(NO) · H$_2$O 2,2-*TT* chain	*trans* –NC–Fe(CN)$_3$(NO)–CN–	*trans*-NiN$_4$N$_2$ Octahedron	[88]
[Cu$_2$(dien)$_2$Fe(CN)$_6$]$_n$ *n*[Cu(dien)(H$_2$O)Fe(CN)$_6$] · 5*n*H$_2$O 2,4 Ribbon	*trans* (–NC–)$_2$Fe(III)(CN)$_2$(–CN–)$_2$ NC–Fe(III)(CN)$_5$	*cis*-CuN$_3$N$_2$ (2 ×) CuN$_3$NO Square pyramids	[48]
[Cu(hatd)(H$_2$O)$_2$]$_n$ 2*n*[Cu(hatd)][Fe(CN)$_6$] · 2*n*H$_2$O 2,2-*TC* chain	*cis* –NC–Fe(III)(CN)$_4$–CN–	*trans*-CuN$_4$O$_2$ *trans*-CuN$_4$N$_2$ Elongated tetragonal bipyramids	[111]
Cu(en)$_2$Fe(CN)$_5$(NO) 2,2-*TT* chain	*trans* –NC–Fe(CN)$_3$(NO)–CN–	*trans*-CuN$_4$N$_2$ Elongated tetragonal bipyramid	[112]
[Cu(teta)(H$_2$O)$_2$] [Cu(teta)Fe(CN)$_6$]ClO$_4$ · 2H$_2$O 2,2-*TT* chain	*trans* –NC–Fe(III)(CN)$_4$CN–	*trans*-CuN$_4$O$_2$ *trans*-CuN$_4$N$_2$ Elongated tetragonal bipyramids	[113]
{Cd(tet)}$_2$Fe(CN)$_6$ · 3H$_2$O 2,4 Chain	*trans* –(NC)$_2$–Fe(II)(CN)$_2$(CN)$_2$–	*cis*-CdN$_4$N$_2$ Octahedron	[14]
[Ph$_4$P]Ni(pn)$_2$Co(CN)$_6$ · H$_2$O 2,2-*TC* chain	*cis* –NC–Co(III)(CN)$_4$–CN–	*trans*-NiN$_4$N$_2$ Octahedron	[55]
[Ni(en)$_2$]$_3$[Co(CN)$_6$]$_2$ · 3H$_2$O 3,2 Ladder	*mer* –NC–Co(III)(CN)$_3$(–CN–)$_2$	*cis*-NiN$_4$N$_2$ Octahedron *trans*-NiN$_4$N$_2$ Octahedron	[91]
[Cu$_2$(dien)$_2$Co(CN)$_6$]$_n$ *n*[Cu(dien)(H$_2$O)Co(CN)$_6$] · 5*n*H$_2$O 2,4 Ribbon	*trans* (–NC–)$_2$Co(III)(CN)$_2$(–CN–)$_2$	*cis*-Cu(1)N$_3$N$_2$ (2 ×) Square pyramid *cis*-Cu(2)N$_3$N$_2$	[89]

coupling and crystal field anisotropy as well as studying the contribution of a given spin mode to a thermodynamic equilibrium property [95]. Subsequent experiments using resonance techniques, namely electron-spin resonance (ESR), nuclear magnetic resonance as well as inelastic neutron scattering yield more detailed information about the energy of spin modes, relaxation mechanisms and spin correlation in the system of interest. If the influence of crystal field anisotropy is to be investigated single crystals of appropriate size are required. It should be stressed, that for correct interpretation of the data detailed knowledge of the crystal structure is necessary. Most of the aforementioned techniques have been applied in the study of magnetic properties of 1D cyanocomplexes.

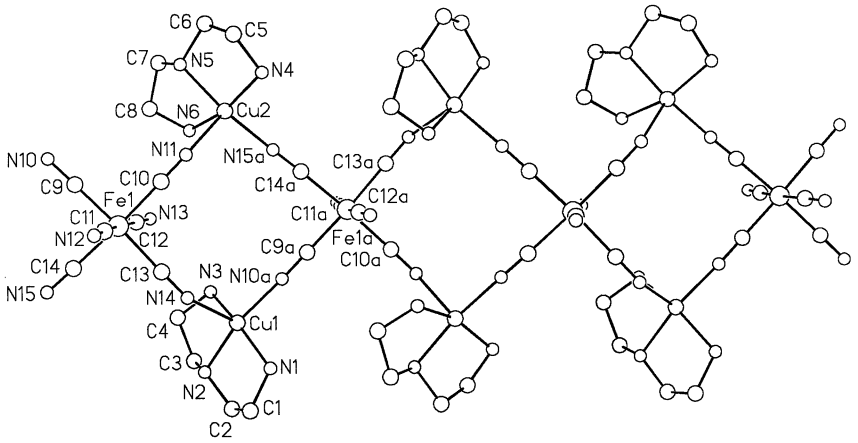


Fig. 6. 2,4 Ribbon-like cation in the structure of $[Cu(dien)]_3[Fe(CN)_6]_2 \cdot 6H_2O$ [48]. Hydrogen atoms are omitted. The dimeric anion $[Cu(dien)(H_2O)–NC–Fe(CN)_5]$ and water molecules of crystallization are not shown.

Cyanocomplex anions as one of the building blocks can be diamagnetic or paramagnetic. The most common cyanocomplex anions are shown in Table 4 along with their spin value. One-dimensional cyanocomplexes according to the magnetic properties of the building blocks can be divided in four groups:

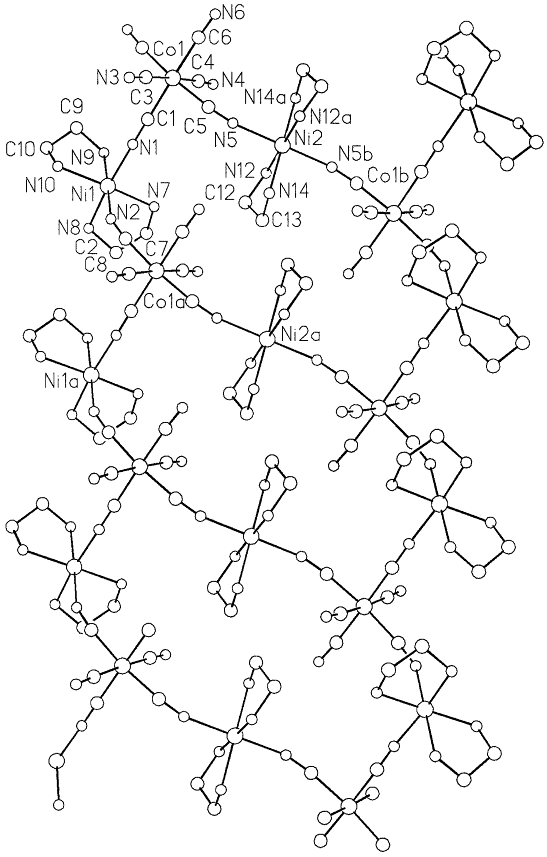


Fig. 7. View of the 3,2 ladder-like structure of $[Ni(en)_2]_3$-$[Co(CN)_6]_2 \cdot 3H_2O$ [91,103]. Hydrogen atoms and water molecules of crystallization are omitted for the sake of clarity.

i. the central atom of the brick (M′) is paramagnetic and the central atom of the cyanocomplex anion (M) (mortar) is diamagnetic;
ii. the central atom of the brick is diamagnetic, but the cyanocomplex anion is paramagnetic;
iii. both central atoms are paramagnetic; and
iv. both central atoms are diamagnetic (this case will not be further discussed).

For the description of the magnetic properties the following Hamiltonian is usually used:

$$H = -J\sum_{i=1}(S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \delta S_i^z S_{i+1}^z) + D\sum_{i=1}(S_i^z)^2 + g\mu_B\vec{H}\sum_{i=1}\vec{S}_i \qquad (1)$$

Table 4
Some cyanocomplex anions and their magnetic properties

$S=0$	$S=1/2$	$S=1$	$S=3/2$
$[Zn(CN)_4]^{2-}$	$[Fe(CN)_6]^{3-}$	$[Mn(CN)_6]^{3-}$	$[Cr(CN)_6]^{3-}$
$[Ni(CN)_4]^{2-}$	$[Mn(CN)_6]^{4-}$	$[Mo(CN)_8]^{4-}$	$[V(CN)_6]^{4-}$
$[Pd(CN)_4]^{2-}$	$[Co(CN)_6]^{4-}$	$[W(CN)_8]^{4-}$	
$[Pt(CN)_4]^{2-}$	$[W(CN)_8]^{3-}$	$[Re(CN)_8]^{3-}$	
$[Co(CN)_6]^{3-}$	$[Ti(CN)_6]^{3-}$		
$[Fe(CN)_6]^{4-}$	$[Ti(CN)_n]^{(n-3)-}$ ($n=6$–8)		
$[Cd(CN)_4]^{2-}$	$[Nb(CN)_8]^{4-}$		
$[Hg(CN)_4]^{2-}$	$[Mo(CN)_8]^{3-}$		
$[Ag(CN)_2]^{2-}$	$[Os(CN)_8]^{3-}$		
$[Ag_2(CN)_3]^{2-}$	$[Co(CN)_5]^{3-}$		
$[Ni(CN)_5]^{3-}$	$[Rh(CN)_6]^{4-}$		
$[Au(CN)_2]^{2-}$			
$[Au(CN)_4]^{-}$			
$[Rh(CN)_6]^{3-}$			
$[Ir(CN)_6]^{3-}$			
$[Ru(CN)_6]^{4-}$			
$[Cu(CN)_n]^{(n-1)-}$ ($n=2$–4)			

The first term describes the anisotropic exchange coupling where J represents exchange coupling constant and δ is the anisotropy of exchange interaction. The notation in Eq. (1) requires J positive for ferromagnetic exchange interaction and J negative for antiferromagnetic exchange interaction. The second term appears due to the uniaxial anisotropy introduced by the crystal field (the so-called single ion anisotropy) where D represents the single-ion anisotropy constant possessing a negative value (easy-axis or Ising anisotropy) or positive value (easy plane anisotropy). The last term characterizes the interaction of the system with an external magnetic field. It is noteworthy that a variety of conventions involving the sign and a factor of 2 before the constant J are often used. For systems with $S = 1/2$, the second term in Eq. (1) vanishes and the crystal field anisotropy is reflected into the anisotropy of exchange coupling [96]. For magnets with real spin $S = 1$ single ion anisotropy appears, while exchange coupling can be considered isotropic. Finally, systems with $S > 1$ usually require consideration of both anisotropic exchange coupling and single ion anisotropy. The survey of cyanocomplex anions with corresponding spin values is presented in Table 1.

In the materials of types (i) and (ii) discussed here the paramagnetic centers are linked always by five atomic bridges, namely in the form of –N≡C–M–C≡N– for the first situation, and in the form of –C≡N–M′–N≡C– for the second one. Consequently, a low value of the exchange coupling constant J can be expected in these types of compounds. The magnetism of compounds containing a magnetic ion with integer spin will be governed by crystal field anisotropy. The magnetic properties of such systems with $S = 1$ possessing strong planar anisotropy D ($D/|J| > 1$) were theoretically investigated by Papanicolaou and Spathis [97]. In this work the concept of (anti)excitons as the elementary excitations from the singlet ground state was proposed. In the ground state spins fluctuate in the easy plane, thus the state is non-magnetic and disordered even at zero temperature. The (anti)excitons could be viewed as the flip of the spin out of the easy plane which can propagate along the chain because of the exchange interaction. Experimental studies of thermodynamic quantities of $\mathrm{Ni(en)_2Ni(CN)_4}$ in the millikelvin temperature range identified the aforementioned material as $S = 1$ Heisenberg antiferromagnetic chain with strong planar anisotropy with $D/k_B = 6$ K and $D/|J| = 7.5$ (k_B is Boltzman constant); the analysis of specific heat below 1 K suggested the existence of (anti)excitons [98]. In 1D cyanocomplexes not only changing the surroundings of the magnetic ion but also modifying the exchange path can influence the type of crystal field anisotropy. For example, unlike $\mathrm{Ni(en)_2Ni(CN)_4}$ characterized by planar anisotropy, ESR studies of $\mathrm{[Ni(en)_2Fe(CN)_5NO]\cdot H_2O}$ carried out by Shyu et al. [88] revealed the presence of a weak easy-axis anisotropy with $D/k_B = -0.45$ K. The susceptibility studies confirmed weak antiferromagnetic exchange coupling in this material yielding $J/k_B = -0.68$ K. $\mathrm{Ni(en)_2Pd(CN)_4}$ represents another material in which easy-axis anisotropy can be expected. The structure of $\mathrm{Ni(en)_2Pd(CN)_4}$ was reported in Ref. [82] and, to our knowledge, the magnetic properties have not yet been studied. Nevertheless, since the magnetic Ni(II) ion is located in the center of a slightly compressed octahedron one could foresee the presence of easy-axis anisotropy in this material [99].

For certain types of ligands the decrease of the symmetry of the crystal field in the brick can be expected. Such an effect was observed in $\mathrm{Ni(bpy)_2Ni(CN)_4}$ where apart from planar anisotropy and exchange coupling also in-plane anisotropy E had to be considered for obtaining consistent values of D, J, E parameters from ESR results and thermodynamic quantities [100].

An interesting example of an $S = 1/2$ 1D cyanocomplex was reported in Ref. [59]. In this work structural and magnetic properties of mixed-valence Cu(II)/Cu(I) complex $\mathrm{Cu(dien)(CN)Cu(CN)_2}$ were investigated. As expected, for these types of materials only weak antiferromagnetic coupling with $J/k_B = -0.68$ K was found.

The low value of the exchange coupling makes 1D cyanocomplexes sensitive to mechanisms responsible for the deviation from 1D behavior. Given that covalent bonds create chain structures the presence of HBs and dipolar coupling may lead to magnetic ordering at non-zero temperature. The HBs linking chains were observed for example in $\mathrm{[Cu(dien)]_3[Fe(CN)_6]_2\cdot 6H_2O}$ [48], and $\mathrm{Cu(en)_2Ni(CN)_4}$ [61]. A specific heat study of the latter material in the millikelvin temperature range revealed that HBs represent alternative exchange paths which in $\mathrm{Cu(en)_2Ni(CN)_4}$, despite its chain structure, lead to quasi-2D magnetic behavior (see Fig. 8). Dipolar coupling was proposed to be responsible for magnetic ordering observed at 120 mK in this material. In contrast, the susceptibility studies of the cyano-bridged heteronuclear complex $\mathrm{[Cu(dien)]_3[Co(CN)_6]_2\cdot 6H_2O}$ revealed that despite the chain structure the magnetic properties are governed by non-interacting Cu dimers [89]. Consequently, for these types of 1D cyanocomplexes the 1D character of the crystal structure does not necessarily mean the same magnetic dimensionality of the system.

Based on the discussion above, 1D cyanocomplexes of types (i) and (ii) are characterized by spin correlations, the study of which require sufficiently low temperatures. In addition, for these materials with integer spins single ion anisotropy should definitely be taken into account before drawing any conclusion about the sign and magnitude of the exchange coupling.

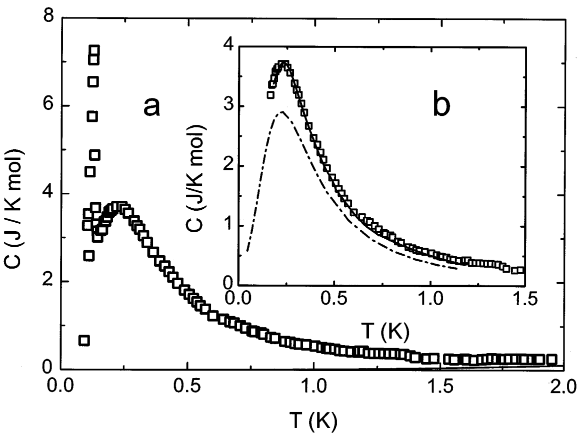


Fig. 8. (a) Temperature dependence of the total specific heat of $Cu(en)_2Ni(CN)_4$ (squares). The lattice contribution is denoted by solid line. (b) Temperature dependence of the magnetic specific heat (squares). The dashed line represents the prediction for Heisenberg antiferromagnetic chain with $J/k_B = -230$ mK, while the solid line denotes the prediction for Heisenberg antiferromagnetic quadratic lattice with $J/k_B = -180$ mK.

Obviously the effects of HBs and dipolar coupling will not be so pronounced in materials of type (iii), which are characterized by an exchange bridge consisting of only one cyano group (two atoms). The presence of two different magnetic ions in the structure gives the possibility to study the magnetic properties of a magnetic chain with alternating spins. Theoretical investigation of the aforementioned systems with antiferromagnetic exchange coupling [101] suggests that the physical mechanism responsible for a non-magnetic ground state in Heisenberg chains possessing a Haldane gap [102] creates a ferromagnetic ground state in alternating chains with antiferromagnetic exchange coupling. Such a material should behave as a ferromagnet at the lowest temperatures and at higher temperatures as an antiferromagnet with an energy gap in the excitation spectrum. Consequently, temperature controlled ferromagnetic–antiferromagnetic crossover is expected in these systems. The aforementioned properties should be universal, regardless of the mutual spin values. To our knowledge the predicted behavior has not been experimentally confirmed yet. An interesting magnetic property of 1D cyanocomplexes containing alternating spins has been reported in Ref. [55]. In this work susceptibility and magnetization studies of $[Ph_4P][Ni(pn)_2M(CN)_6]\cdot H_2O$ (M = Fe, Cr) revealed the presence of intrachain ferromagnetic coupling resulting from the strict orthogonality of the magnetic orbitals located on the adjacent Ni(II) and M(III) ions. The same mechanism is responsible for the intrachain ferromagnetic coupling in $[Et_4N]_2[Mn(acacen)Fe(CN)_6]$ [52] and $[Ni(en)_2]_3[M(CN)_6]_2\cdot 3H_2O$ [103] (this compound was originally claimed as a dihydrate by Ohba et al. [103]; however, the structural redetermination by Eriksen et al. [91] revealed it to be a trihydrate).

Compounds of type (iii), consisting of uniform spins, have also been synthesized and studied. An unexpected ferromagnetic behavior in $[Fe(cyclam)][Fe(CN)_6]\cdot 6H_2O$, linear chain with alternating $[Fe(CN)_6]^{3-}$ and $[Fe(III)(cyclam)]^{3+}$ units was reported in Ref. [45]. As the authors suggested, in this material ferromagnetic coupling with $J/k_B = 12.4$ K arose due to the orthogonality of the d_{xy} orbital (b_{2g}) on Fe from the $[Fe(CN)_6]^{3-}$ anion and the d_{xz} and d_{yz} orbitals (t_{2g}) on Fe(III) from $[Fe(III)(cyclam)]^{3+}$.

6. Conclusions

Current extensive effort devoted to the synthesis and characterization of 1D cyanocomplexes confirms that the chemistry of these compounds represents a growing field of interest. Different types of 1D cyanocomplexes have been prepared and characterized. For their preparation the brick and mortar method can be used. The compounds studied display great variability with respect to type and composition and their structure can be described using the concept of connectedness. Crystal structures of 56 1D cyanocomplexes were determined by single crystal structure analysis, among these 42 contain at least one paramagnetic ion and 14 were diamagnetic. Up to now no cyanocomplexes built up of paramagnetic anion and diamagnetic cation (group (ii)) have been characterized structurally. The 1D cyanocomplexes studied contained mostly dicyanoargentate, tetracyanonickelate and various hexacyanometallate anions. The possibilities to prepare 1D cyanocomplexes with coordination numbers 3, 5, 7 and higher were not explored fully.

As far as magnetic properties are concerned, 1D cyanocomplexes are characterized by divers magnetic properties resulting from their structures. The low values of their exchange coupling makes them suitable for experimental investigation of systems with strong crystal field anisotropy, systems with comparable exchange and dipolar coupling and potentially Heisenberg antiferromagnetic chains with alternating spins. The data published indicate that structurally 1D cyanocomplexes are suitable representatives for the study of magnetic properties of quantum spin chains despite the fact that their behavior sometimes deviates from magnetically 1D character.

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