

A Zinc(II)-Silver(I) Bimetallic Coordination Polymer Assembled Through Argentophilic and π - π Interactions, $\{[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})\{\text{Ag}(\text{CN})_2\}][\text{Ag}(\text{CN})_2]\cdot\text{MeOH}\}_n$ (phen = 1,10-Phenanthroline)

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A cyanido-bridged Zn(II)-Ag(I) bimetallic coordination polymer, $\{[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})\{\text{Ag}(\text{CN})_2\}][\text{Ag}(\text{CN})_2]\cdot\text{MeOH}\}_n$ (**1**), was prepared using ZnCl_2 , 1,10-phenanthroline (phen) and $\text{K}[\text{Ag}(\text{CN})_2]$ and characterized by IR spectroscopy, thermal analysis and X-ray crystallography. The crystal structure of **1** consists of dinuclear $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})\{\text{Ag}(\text{CN})_2\}]^+$ cations, $[\text{Ag}(\text{CN})_2]^-$ anions and a methanol molecule. The non-coordinated $[\text{Ag}(\text{CN})_2]^-$ anions are linked to the $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})\{\text{Ag}(\text{CN})_2\}]^+$ complex cations through argentophilic interactions leading to the formation of chains. The chains are connected by hydrogen bonds and π - π interactions to give a 3D network.

Key words: Zinc(II), Silver Cyanide, 1,10-Phenanthroline, Coordination Polymer

Introduction

Due to the ambidentate nature of CN^- , transition metal cyanides such as $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ag}(\text{CN})_2]^-$ have been widely used as building blocks for the preparation of coordination polymers with one-, two- or three-dimensional networks [1–25]. The structural stability is an important factor in the study of the microporous functions of coordination polymers [26]. Therefore, due to their high stability, cyanidometalates may find extensive applications as microporous materials. The coordination polymers of coinage metal cyanides are of great interest in this respect because the unusually low 2-coordination of the metal centers allows them to reversibly adsorb nucleophiles offering applications in separations and sensing technologies [27]. Another unique feature of these structures is that the central silver or gold atoms are capable of forming d^{10} - d^{10} M–M bonds, which are useful tools in crystal engineering of polymeric structures [9–11, 15–25]. Several recent reviews have been devoted to the chemistry of cyanido-bridged metal complexes illustrating the popularity of these systems [1, 12–14].

The metal-cyanide units, *e.g.*, $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ni}(\text{CN})_4]^{2-}$, are usually preserved in supramolecular assemblies. The $[\text{Ag}(\text{CN})_2]^-$ unit in many cases also remains preserved [19, 20, 22–24, 28, 29], but sometimes it may undergo secondary reactions forming a variety of products consisting of $[\text{Ag}_2(\text{CN})_3]^-$ [25], $[\text{Ag}(\text{CN})_2]_5^-$ [8] and $[\text{Ag}_3(\text{CN})_5]^{2-}$ anions [21]. We present here the structural characterization of a novel cyanido-bridged Zn(II)–Ag(I) 1D coordination polymer $\{[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})\{\text{Ag}(\text{CN})_2\}][\text{Ag}(\text{CN})_2]\cdot\text{MeOH}\}_n$ (phen = 1,10-phenanthroline), assembled by significant argentophilic interactions. The chains are extended through hydrogen bonds and π - π interactions to give a 3D network.

Experimental Section

Materials

ZnCl_2 and 1,10-phenanthroline (phen) were obtained from Merck Chemical Co./Germany. AgNO_3 was a product of Panreac/Spain. $\text{K}[\text{Ag}(\text{CN})_2]$ was prepared by reacting AgNO_3 with KCN in a 1 : 2 mol ratio in water.

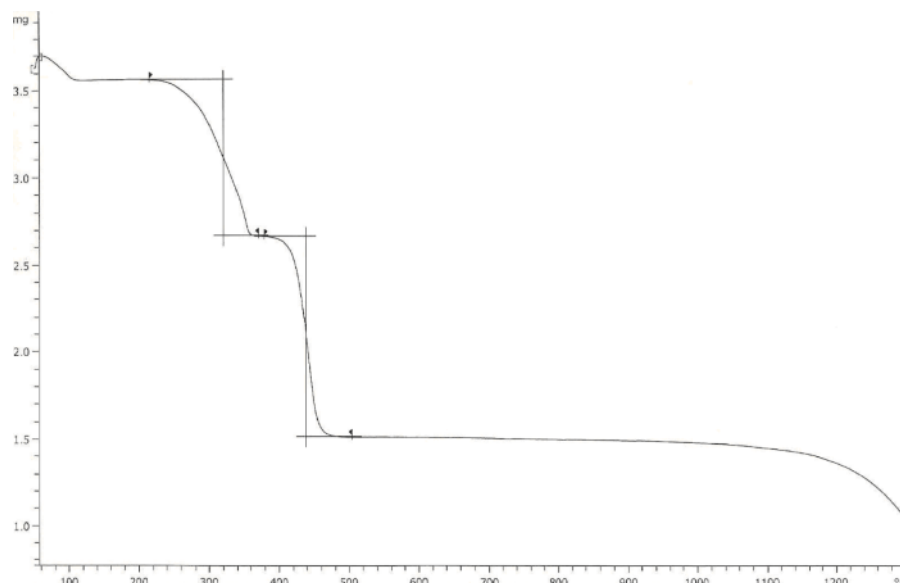


Fig. 1. TGA curve of $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})\{\text{Ag}(\text{CN})_2\}][\text{Ag}(\text{CN})_2]$ (precipitated product of **1**).

Synthesis

To a solution of 1 mmol (0.136 g) ZnCl_2 in 10 mL water was added 2 mmoles of 1,10-phenanthroline (phen) in 15 mL methanol. After stirring for 15 min, 2 mmoles of $\text{K}[\text{Ag}(\text{CN})_2]$ in 15 mL distilled water were added and the reaction mixture was stirred for further 30 min at room temperature. After filtration, the residue was collected and dried in air. Crystals of **1** were obtained by dissolving some of the precipitated product in a 1 : 1 water-methanol mixture on heating and keeping the filtrate in air for over night. The crystals were washed with methanol and finally dried in air. M. p.: 283–284 °C. – IR: $\nu = 1618, 1589$ (C=N), 1505, 1423 (C=C), 2163, 2138 $\nu(\text{C}\equiv\text{N}) \text{ cm}^{-1}$.

IR and thermal measurements

The IR spectra of the samples were recorded with a Perkin Elmer FTIR spectrophotometer using KBr pellets in the 4000–500 cm^{-1} range. The solid-state thermal gravimetric analysis (TGA) of the bimetallic complex was carried out on a Mettler Toledo TGA/SDTA 851e analyzer under argon atmosphere at the heating rate of 10 °C min^{-1} .

X-Ray structure determination

X-Ray diffraction data of **1** were collected with an Oxford Gemini S diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 110 K. The structure was solved by Direct Methods with SHELXS-97 [30] and refined by full-

matrix least-squares procedures on F^2 using the program SHELXL-97 [30]. All non-hydrogen atoms were refined anisotropically. Crystal data and details of the data collection and structure refinement are summarized in Table 1.

Table 1. Crystal data and details of data collection and refinement for complex **1**.

Formula	$\text{C}_{29}\text{H}_{22}\text{Ag}_2\text{N}_8\text{O}_2\text{Zn}$
Formula weight	795.66
Crystal size, mm^3	$0.2 \times 0.2 \times 0.1$
Temperature, K	110(2)
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a , \AA	10.3619(5)
b , \AA	12.0360(5)
c , \AA	12.3670(6)
α , deg	109.019(4)
γ , deg	91.090(4)
γ , deg	99.812(4)
V , \AA^3	1432.22(11)
Z	2
ρ_{calcd} , g cm^{-3}	1.85
$\mu(\text{MoK}\alpha)$, mm^{-1}	2.2
$F(000)$, e	784
2θ range, deg	2.95–25.00
h, k, l limits	–12 : 12, –14 : 14, –11 : 14
Transmission max. / min.	1.0 / 0.82
Refl. collected / unique / R_{int}	8839 / 4987 / 0.0223
Refl. “observed” with $I > 2\sigma(I)$	4061
Data / restraints / ref. parameters	4987 / 2 / 390
R_1 / wR_2 / S (all data)	0.0397 / 0.0759 / 0.0959
Largest diff. peak / hole, e \AA^{-3}	1.84 / –0.71

CCDC 865561 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The title complex was prepared by the reaction of ZnCl_2 , 1,10-phenanthroline (phen) and $\text{K}[\text{Ag}(\text{CN})_2]$

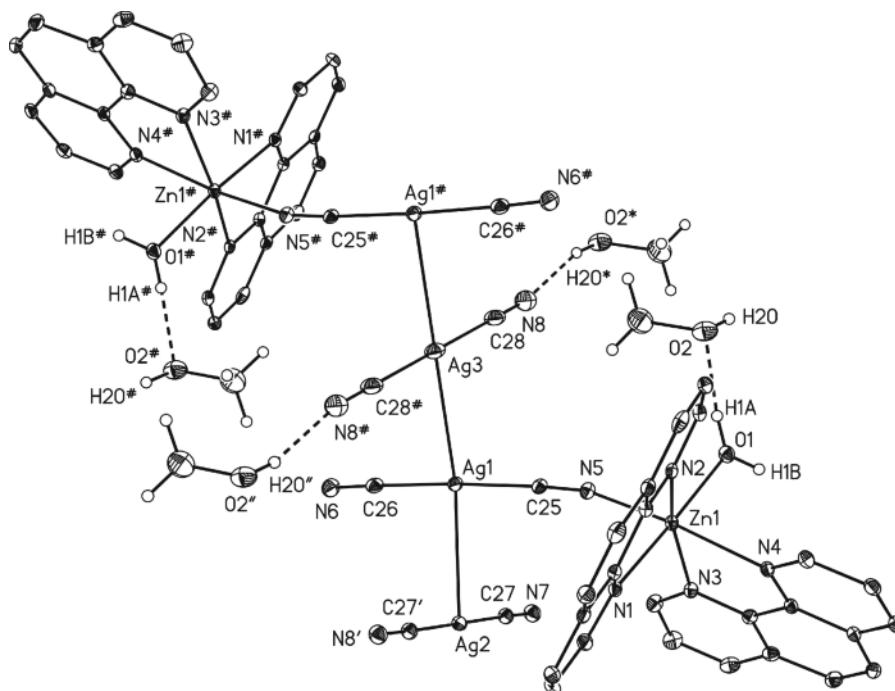


Fig. 2. Graphical representation of a selected part of the chains formed by **1** in the solid state due to argentophilic interactions including MeOH molecules attached to the chains by hydrogen bonds. All C-bonded hydrogen atoms of the phen ligands are omitted for clarity. Symmetry codes: (') $-x+1, y, -z+1/2$; (#) $x, -y+1/2, -z+3/2$; (*) $3-x, -y, -z$; (") $x-1, y, z$.

Bond lengths		Bond angles	
Ag(1)–C(26)	2.063(4)	C(26)–Ag(1)–C(25)	177.63(14)
Ag(1)–C(25)	2.064(4)	C(27)–Ag(2)–C(27)'	180
Ag(1)–Ag(2)	3.0463(3)	C(28)–Ag(3)–C(28)#	180
Ag(1)–Ag(3)	3.0697(3)	C(25)–Ag(1)–Ag(2)	87.14(10)
Ag(2)–C(27)	2.059(4)	C(26)–Ag(1)–Ag(2)	90.52(11)
Ag(2)–C(27)'	2.059(4)	N(2)–Zn(1)–N(1)	77.77(11)
Ag(2)–Ag(1)'	3.0463(3)	N(3)–Zn(1)–N(1)	95.88(11)
Ag(3)–C(28)	2.061(6)	N(1)–Zn(1)–N(4)	92.14(11)
Ag(3)–C(28)#	2.061(6)	N(5)–Zn(1)–N(1)	89.28(12)
Ag(3)–Ag(1)#	3.0697(3)	N(3)–Zn(1)–N(2)	162.07(11)
Zn(1)–O(1)	2.077(3)	N(5)–Zn(1)–N(2)	102.25(11)
Zn(1)–N(1)	2.165(3)	N(5)–Zn(1)–N(3)	94.34(12)
Zn(1)–N(2)	2.161(3)	N(5)–Zn(1)–N(4)	170.52(11)
Zn(1)–N(3)	2.147(3)	O(1)–Zn(1)–N(2)	92.96(11)
Zn(1)–N(4)	2.247(3)	O(1)–Zn(1)–N(3)	92.65(11)
Zn(1)–N(5)	2.096(3)	O(1)–Zn(1)–N(4)	86.18(11)
N(1)–C(1)	1.316(5)	O(1)–Zn(1)–N(5)	93.89(12)
N(1)–C(12)	1.350(5)	C(25)–N(5)–Zn(1)	166.0(3)
N(5)–C(25)	1.145(5)	N(5)–C(25)–Ag(1)	176.7(3)
N(6)–C(26)	1.142(5)	N(6)–C(26)–Ag(1)	177.9(4)
N(7)–C(27)	1.151(5)	N(7)–C(27)–Ag(2)	177.4(4)
N(8)–C(28)	1.126(6)	N(8)–C(28)–Ag(3)	179.0(5)

Table 2. Selected bond lengths (Å) and bond angles (deg) for compound **1**^a.

^a Symmetry codes: (') $-x+1, y, -z+1/2$; (#) $x, -y+1/2, -z+3/2$.

mixed in a molar ratio of 1 : 2 : 2. In the IR spectrum of the residual product (not of the crystals) of complex **1**, two $\nu(\text{CN})$ bands are observed, one at 2163 cm^{-1} and the other one at 2138 cm^{-1} , while for $\text{K}[\text{Ag}(\text{CN})_2]$ only one $\nu(\text{C}\equiv\text{N})$ appears at 2140 cm^{-1} . The presence of two bands indicates that the complex contains both bridging and terminal cyanide groups. Generally, the stretching frequency of the terminal cyanide

is lower relative to that of bridging ones [17, 28, 31]. In the IR spectrum of 1,10-phenanthroline the characteristic bands observed are $\nu(\text{C}=\text{N})$ at 1618 and 1589 cm^{-1} , and $\nu(\text{C}=\text{C})$ at 1505 and 1423 cm^{-1} . For **1** the $\nu(\text{C}=\text{N})$ vibrations of phen were observed at 1626 and 1579 cm^{-1} , while the $\nu(\text{C}=\text{C})$ bands appeared at 1505 and 1424 cm^{-1} . The presence of these bands indicates the coordination of phen to the metal.

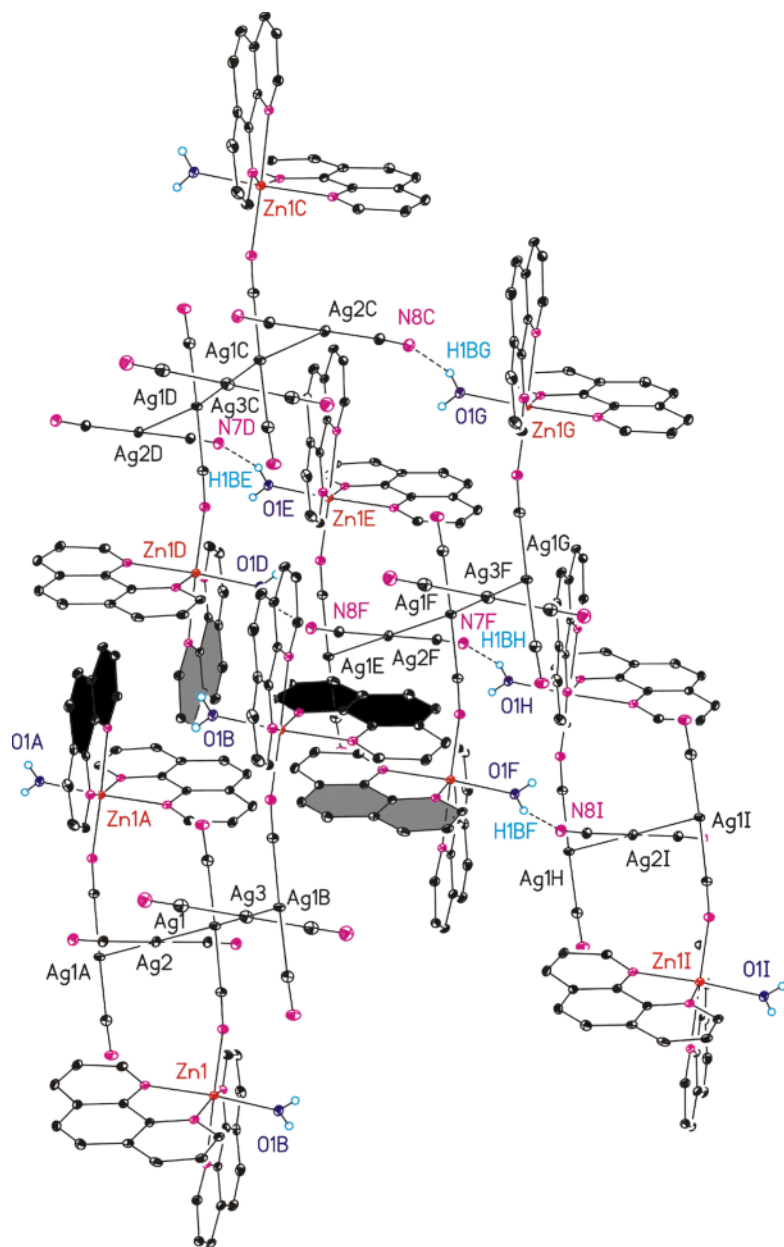


Fig. 3a (color online). Selected part of the 3D network of **1** in the solid state. Hydrogen bonds are indicated by dotted lines. π - π -Interacting aromatic rings are filled with black and gray colors. MeOH molecules and C-bonded hydrogen atoms are omitted. Labels 'A' to 'I' refer to the first to the ninth symmetry-generated asymmetric unit of **1**.

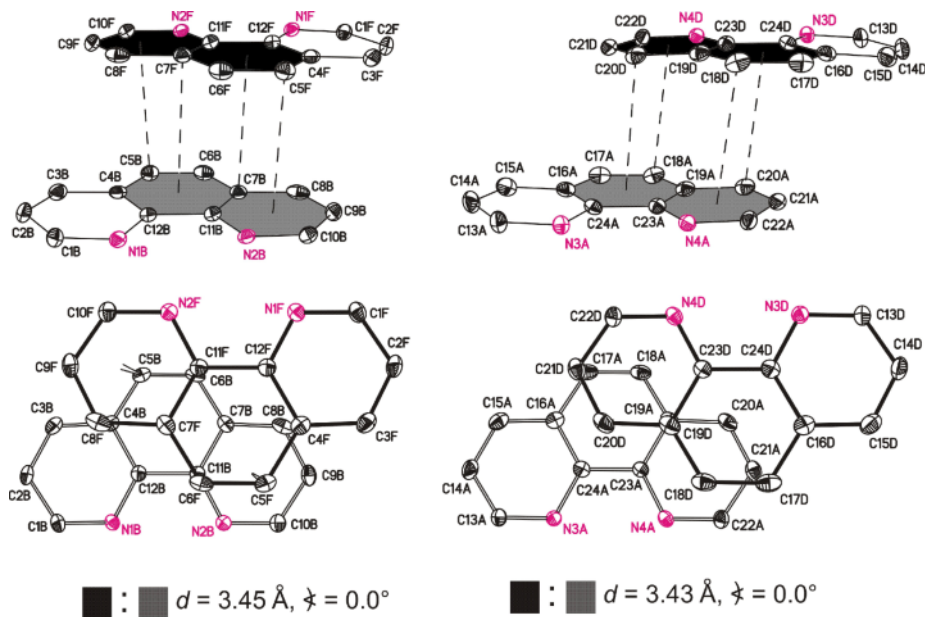


Fig. B (color online). Graphical illustration of the parallel-displaced sandwich-type π - π interactions of phen ligands in **1** in the solid state, where d gives the distances of interacting phen ligands and the interplanar angles, respectively. Labelling refers to the code given in Fig. 3a.

Thermal studies

The results of the thermogravimetric analysis indicate a good correlation between the calculated and found weight loss values for the investigated complex. The thermal decomposition of the precipitated product of **1** (not of crystals) is shown in Fig. 1. The decomposition starts at 60 °C and occurs in three steps. At the first stage water is released corresponding to the weight loss of 1.9% (calcd. 2.35%) between 60 and 120 °C. The second weight loss of 24.7% in the range 220–365 °C can be explained by the removal of one phen molecule (calcd. 23.57%). The next weight loss of 31.8% (calcd. 37.19%) takes place in the range of 370–500 °C due to the release of the remaining phen and four CN⁻ ligands. Cyanide is usually released in the temperature range of 400–500 °C [31, 32]. The release of these two groups is associated with two exothermic transitions at 337 and 468 °C, respectively, in the DSC. There is also one endothermic transition in DSC at 283 °C corresponding to the melting point of the complex. The residual mass of ~41% is consistent with the predicted value of 38.91% for ZnO + 2Ag. These observations suggest that the proposed formula of the complex is [Zn(phen)₂(H₂O){Ag(CN)₂}] [Ag(CN)₂], which reflects that the precipitated product of **1** (before crystallization) does not contain methanol.

Crystal structure description of **1**

The molecular structure of the asymmetric unit of **1** along with the crystallographic numbering scheme is illustrated in Fig. 2. Selected bond lengths and bond angles are listed in Table 2. The crystal structure of the complex consists of [Zn(phen)₂(H₂O){Ag(CN)₂}]⁺ cations, [Ag(CN)₂]⁻ anions and one molecule of methanol. The Zn(II) ions are coordinated to four nitrogen atoms of phen ligands, one water molecule and one [Ag(CN)₂]⁻ ion assuming a slightly distorted octahedral geometry. The *cis*-N–Zn–N angles vary from 89.31(14) to 90.59(14)°, while the *trans*-N–Zn–N angle is 179.31(14)°. The *cis*-N–Zn–N(CN) angles are larger than the *cis*-N–Zn–N(phen) angles. The Zn–N≡C unit is nearly linear with a bond angle of 166.0(3)°. The coordination environments of the coordinated and non-coordinated [Ag(CN)₂]⁻ ions are close to linear (Ag–C–N = 176.7(3)–179.0(5)°). The cyanido groups are bent away from each other so that the silver(I) ions reach the closest contacts between the [Ag(CN)₂]⁻ anions. The Zn–N bond lengths, 2.096(3)–2.247(3) Å, are comparable to those in known structures, *e.g.*, in [Zn(phen)₃]Cr₂O₇·4H₂O [33].

The coordinated and noncoordinated [Ag(CN)₂]⁻ ions are linked to each other through argentophilic interactions. The Ag–Ag interactions are extend-

ing in one dimension forming a zigzag chain as shown in Fig. 2. The Ag–Ag distances ranging from 3.0463(3)–3.0697(3) Å are below the sum of the van der Waals radii of two silver atoms (3.44 Å), which is considered to be the upper limit of the distance for viable argentophilic d^{10} - d^{10} interactions [8, 25, 34]. The Ag1–Ag2–Ag1A and Ag2–Ag1–Ag2A angles involved in this bonding are 153.411(14) and 179.998(1)° respectively. The corresponding Ag···Ag distances in some similar reported complexes are 3.289 Å for [Ni(en)₂Ag(CN)₂]{Ag(CN)₂} [24], 3.1580 Å for [Cu(en)₂Ag(CN)₂]{Ag(CN)₂} [20], 3.221 Å for [Zn(en)₂Ag(CN)₂]{Ag(CN)₂} [19], and 3.1750 Å for [Cd(en)₂Ag(CN)₂]{Ag(CN)₂} [23].

In the crystal structure the chains do interact with each other by both hydrogen bonding and π - π contacts (Fig. 3a). Selected data of the hydrogen bonds are

Table 3. Selected bond lengths (Å) and angles (deg) of hydrogen bonds of **1**.

Donor–H···Acceptor	D···A	\angle (D–H···A)
O1–H1A···O2	2.649(5)	161(7)
O1–H1B···N7	2.813(4)	157(6)
O2–H2O···N8	2.752(5)	164(6)

given in Table 3, whereas Fig. 3b illustrates the π - π interactions in more detail.

The results of present study have shown that [Ag(CN)₂][−] can be used as a bridging ligand as well as a counter-ion in the formation of polymetallic complexes. Argentophilic interactions play a significant role in increasing the dimensionality of such complexes [19–25]. We have isolated and crystallographically characterized a rare example of a 1D coordination polymer (**1**), assembled by such interactions.

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