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Nitrate and nitrite silver complexes with weakly coordinating nitriles

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The contribution is dedicated to Prof. Dr. hab. Antoni Grodzicki on the occasion of his 85th Birthday.

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ABSTRACT

The structures and luminescent properties of silver(I) complexes with weakly coordinating nitrile ligands: 1,4-dicyanobenzene (1,4-dcb) and 3-cyanopyridine (3-cpy) and nitrite or nitrate coordination are investigated. One molecular complex [Ag(3-cpy)$_2$(NO$_2$)], one 1-D coordination polymer [Ag(3-cpy)$_2$NO$_3$]$_\infty$ and two rare 2-D [Ag$_3$(3-cpy)$_2$(NO$_2$)$_3$]$_\infty$ and 3-D [Ag$_2$(1,4-dcb)(NO$_3$)$_2$]$_\infty$ coordination polymers are described. Coordination of the luminescent ligands does not enhance their emission properties, however extension of coordination network may lead to new emission bands in the visible region.

1. Introduction

R—C≡N are isolectronic with several other unsaturated ligands *e.g.* alkynes, nitrogen or carbon monoxide. Though in some inorganic chemistry textbooks they are introduced as excellent donors [1], the authors of this paper share the more widespread view that organic nitriles are rather poor σ-donors and π-acceptors and so-called "temporary ligands" [2–4]. Nitriles are weak bases due to the sp hybridization of the nitrogen atom and the high s character, which does not favor the electron pair sharing with acids – either Bronsted (proton) or Lewis (metal cations) [5]. Gas phase basicities of nitriles (acetonitrile, 1,3-dicyanobenzene) are between those of phosphine PH$_3$ and benzyl alcohol [6] whereas the coordination ability of acetonitrile towards transition metal cations was placed between that of ethylene glycol and trifluoroacetic acid (neutral form); towards lanthanides it is even weaker complexing agent comparable to dichloromethane [7]. Nitriles can be easily displaced from metal complexes by other species (ligands, substrates etc.) and hence the usefulness of nitriles as complexing agents is mainly associated with their labile coordination mode and ability to serve as convenient precursors for a variety of coordination/metalorganic compounds [8]. Interesting idea how to utilize the lability of nitrile complexes comes from the paper of Han and co-workers who studied silver(I) coordination polymers with bridging nitrile ligands as antimicrobial agents releasing Ag$^+$ ions [9].

The coordination mode of nitriles is usually η^1 with the M—N≡C angle close to linear but there are some examples of side-on η^2 nitrile complexes [10]. Coordination of nitriles to metal centers may change the charge distribution within the nitrile moiety and alter the reactivity of coordinated nitrile leading to the formation of several products [2,3,8,10].

Despite some obstacles described in the previous paragraph multifunctional nitriles were succesfully applied as bridging ligands in the construction of coordination polymers [9,11–20]. Among them there are several example of silver complexes [9,11,14,19,21]. In addition to the above-mentioned antimicrobial activity, guest-adsorption properties of Ag(I) coordination polymers with 1,4-dicyanobenzene towards toluene and xylenes were described [21].

Our intention was to investigate the structure and potential luminescent properties of coordination polymers of silver with nitrile ligands and nitrite/nitrate coordination [*e.g.* 22–24]. Especially nitrite ion exhibits a variety of coordination modes in metal complexes [*e.g.* 25–28]. As linkers we have applied 1,4-dicyanobenzene and 3-cyanopyridine, which are known to have acted both as monodentate or bidentate bridging ligand [20,29–35]. We have managed to isolate four

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compounds including relatively rare polydimensional silver(I) coordination polymers [9,11,14,15,19,21,22,33,36–39] and we describe their synthesis, structure and luminescent properties in the following chapters.

2. Experimental

2.1. General information about the chemicals

Silver(I) nitrite(III) was prepared according to the reported procedure [40]: briefly silver(I) nitrate(V) (12 g, 0.07 mol) was dissolved in 13 mL of hot water and sodium nitrite(III) (7 g, 0.01 mol) solution in 7 mL of water was added to it. The mixture was stirred and cooled down followed by the precipitation of yellow needles. The product was washed with cold, distilled water, dried, and stored in a dark place (silver compounds are light-sensitive). The following chemicals were used as purchased: silver(I) nitrate(V) $AgNO_3$, p.a., POCh; sodium nitrite (III) $NaNO_3$, p.a., B&K; 3-cyanopyridine (3-cpy), 97%, Fluka AG; 1,4-dicyanobenzene (1,4-dcb), 98%, ACROS ORGANICS; acetonitrile, 99,9%, Merck; toluene and methanol, p., POCh; ethanol, 99.8%, POCh.

2.2. Synthetic procedures

2.2.1. $[Ag(3\text{-cpy})_2(NO_2)]$ (**1**)

Compound **1** was synthesized by the addition of 3-cyanopyridine (0.12 g, 0.0012·mol) in acetonitrile (4 mL) to $AgNO_2$ (0.09 g, 0.00058·mol) solution in hot water (8 mL). The reaction mixture was stirred and left for crystallization. A colorless crystalline product was obtained in the form of needles, yield 0.1324 g, 63%; m.p. 117 °C. Elemental analysis of $C_{12}H_8AgN_5O_2$: calcd N 19.34, C 39.80, H 2.23; found N 19.20, C 39.80, H 2.21. FT-IR (crystalline product): 3100 (w), 3073 (w), 3024 (w), 2233 (s), 1591 (s), 1566 (w), 1474 (m), 1416 (s), 1269 (s), 1235 (m), 1245 (m), 1182 (vs), 1121 (w), 1039 (w), 1028 (w), 810 (s), 692 (vs), 640 (w), 554 (w) cm^{-1}.

2.2.2. $[Ag_3(3\text{-cpy})_2(NO_2)_3]_\infty$ (**2**)

Compound **2** was synthesized in the same way as a complex **1** but with the different amount of 3-cyanopyridine (0.04 g, 0.00038 mol), colorless crystalline product was obtained in the form of blocks, yield 0.0592 g, 45%; m.p. 138 °C. Elemental analysis of $C_{12}H_8Ag_3N_7O_6$: calcd N 14.64, C 21.52, H 1.20; found N 14.56, C 21.46, H 1.25. FT-IR (crystalline product): 3105 (w), 3069 (w), 3027 (w), 2245 (m), 1589 (m), 1567 (w), 1474 (m), 1417 (m), 1249 (s), 1238 (vs), 1208 (s), 1191 (s), 1120 (m), 1064 (w), 1040 (m), 1028 (m), 937 (w), 845 (w), 812 (m), 789 (w), 696 (m), 639 (w) cm^{-1}.

2.2.3. $[Ag(3\text{-cpy})_2NO_3]_\infty$ (**3**)

Compound **3** the $AgNO_3$ (0.287 g, 0.00169 mol) was dissolved in ethanol (5 mL) and stirred until completely dissolved. The solution of 3-cyanopyridine (0.176 g, 0.00169 mol) in toluene (5 mL) was added to a solution of $AgNO_3$. The reaction mixture was stirred. After that the solvent was evaporated and recrystallization from the methanol (5 mL) afforded colorless crystals, yield 0.210 g, 66% (with regard to 3-cyanopyridine) m.p. 160–163.5 °C. Elemental analysis of $C_{12}H_8AgN_5O_3$: calcd N 18.52, C 38.12, H 2.13, found N 18.38, C 38.03, H 2.32. FT-IR (crystalline product): 3284 (w), 3167 (w), 3105 (w), 3069 (m), 3033 (m), 2988 (w), 2233 (m), 1645 (m), 1594 (w), 1475 (w), 1445 (w), 1428 (m), 1317 (vs), 1241 (s), 1194 (s), 1110.31 (m), 1040.61 (m), 1030.97 (m), 950.53(w), 935.35 (w), 814.94(m), 708.00 (w), 689.87(m), 649.16 (w) cm^{-1}.

2.2.4. $[Ag_2(1,4\text{-dcb})(NO_3)_2]_\infty$ (**4**)

Compound **4** was synthesized by the addition of a solution of 1,4-dicyanobenzene (0.075 g, 0.00059 mol) in toluene (5 mL) to a solution of $AgNO_3$ (0.1 g, 0.00059 mol) in ethanol (5 mL). The reaction mixture was stirred and left for crystallization. A colorless crystalline product was obtained, yield 0.1040 g, 75%, m.p. 171–174 °C. The molecular formula $C_8H_4Ag_2N_4O_6$: calcd N 11.97; C 20.54; H 0.86; found N 11.50, C 20.22, H 0.85. FT-IR (crystalline product): 3105 (w), 3070 (m), 3033 (w), 2988 (w), 2234 (m), 1745 (w), 1595 (m), 1572 (w), 1476 (w), 1429 (s), 1408 (w), 1372 (s), 1355 (m), 1350 (vs), 1194 (w), 1067 (w), 1043 (w), 1032 (m), 936 (w), 815 (m), 691 (m), 651 (w), 557 (w), 475 (w) cm^{-1}.

2.3. Instrumental methods

The FT-IR was recorded with FT-IR Nicolet iS50 with built-in Thermo Scientific diamond ATR. All spectra were performed and formatted by OMNIC software. Measurements were performed in solids for solvent-free crystals. Excitation and emission spectra of the solid samples were registered at room temperature in a F-7000 Hitachi Fluorescence Spectrophotometer equipped with a xenon flash lamp. The elementary CHNS analyses were performed on a Vario EI Cube Elemental Analyzer. The melting points of the compounds were determined by Stuart Scientific SMP3.

2.4. Crystallography

The crystal structure data were collected on an IPDS 2T dual beam diffractometer (STOE & Cie GmbH, Darmstadt, Germany) at 120.0(2) K with MoK_α radiation of a microfocus X-ray source (GeniX 3D Mo High Flux, Xenocs, Sassenage, France). Crystals were cooled using a Cryostream 800 open flow nitrogen cryostat (Oxford Cryosystems). Data collection and image processing was performed with X-Area 1.75 [41]. Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method). The structures were solved using intrinsic phasing procedure implemented in SHELXT and all non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least squares procedure based on F2 using the SHELX–2014 program package [42]. The Olex [43] and Wingx [44] program suites were used to prepare the final version of CIF files. Olex [43] and Mercury [45] were used to prepare the figures. Hydrogen atoms were refined using isotropic model with $U_{iso}(H)$ values fixed to be 1.2 times U_{eq} of the carbon atoms to which they were attached. In the crystal structure of **2** the atom Ag2 and nitrite O3–N2–O4 were modelled as disordered 50/50 over special positions they occupy. A summary of crystallographic data is shown in Table 1. CSD deposition Numbers **2153985–2153988** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Synthesis

As a result of the relatively simple syntheses we have obtained one molecular complex **1** and three coordination polymers **2**–**4**, which are presented in Scheme 1. In the reaction of silver nitrite with the 3-cyanopyridine we have initially used the molar ratio $AgNO_2$:3-cpy of 1:1 and we noticed the two forms of crystals: blocks and needles that formed in the same reaction mixture. We measured the crystal structures of those two products and subsequently we changed the ratio of the reagents in such a way that it matched the ratio in the final products. It was sufficient to isolate **1** and **2** in a pure form at molar ratios $AgNO_2$:3-cpy 1:2 and 3:2 respectively.

Since complex **1** is molecular and may be used as a precursor to other silver nitrite complexes we investigated its solubility in several solvents. It dissolved without decomposition only in polar solvents such as ethanol and acetonitrile and did not dissolve (or poorly) in diethyl ether, toluene or *n*-hexane.

With the intention of comparing the silver nitrite and silver nitrate complexes we have also carried out the reaction of silver nitrate with 3-

Table 1
Crystallographic data for compounds **1–4**.

Complex	1	2	3	4
Formula	$C_{12}H_8AgN_5O_2$	$C_{12}H_8Ag_3N_7O_6$	$C_{12}H_8AgN_5O_3$	$C_4H_2AgN_2O_3$
Formula weight	362.1	669.86	378.1	233.95
Temperature (K)	120(2)			
Wavelength (Å)	0.71073			
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	P-1	$C2$	$P2_1/c$
a (Å)	3.76176(12)	7.2751(9)	27.298(3)	3.7339(7)
b (Å)	23.6955(6)	8.0268(9)	6.4604(5)	17.938(6)
c (Å)	14.2655(4)	8.5796(8)	3.6513(4)	8.9505(19)
α (°)	90	103.035(8)	90	90
β (°)	96.174(3)	90.919(9)	93.091(10)	96.025(16)
γ (°)	90	113.904(8)	90	90
V (Å)	1264.21(7)	442.98(9)	642.99(12)	596.2(3)
Z	4	1	2	4
Crystal size (mm)	0.31 × 0.13 × 0.04	0.15 × 0.12 × 0.06	0.14 × 0.10 × 0.07	0.30 × 0.18 × 0.07
$T_{\min}$, $T_{\max}$	0.731, 0.962	0.656, 0.829	0.844, 0.917	0.712, 0.893
μ (mm^{-1})	1.60	3.33	1.59	3.32
Absorption correction	Integration			
Reflections collected/unique/unique[I > 2r(σ)]	13349/2493/2210	5841/1734/1607	3645/1262/1255	3491/1155/1081
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.617	0.617	0.616	0.617
R_{int}	0.043	0.029	0.042	0.024
Data/restraints/parameters	2493/0/181	1734/0/145	1262/0/97	1155/0/91
Goodness of fit (GOOF) on F^2	1.053	1.045	1.091	1.054
Final R indices [I > 2r(σ)]	$R_1 = 0.031$ $wR_2 = 0.083$	$R_1 = 0.019$ $wR_2 = 0.046$	$R_1 = 0.038$ $wR_2 = 0.103$	$R_1 = 0.018$ $wR_2 = 0.047$
R indices (all data)	$R_1 = 0.035$ $wR_2 = 0.085$	$R_1 = 0.021$ $wR_2 = 0.047$	$R_1 = 0.039$ $wR_2 = 0.103$	$R_1 = 0.020$ $wR_2 = 0.048$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.65 /−0.94	0.83 /−0.45	0.57/−0.89	0.37 /−0.47

cyanopyridine and in this way we have produced the known 1-D coordination polymer **3** as the unique product [33].

On the other hand we did not succeed with similar comparison for 1,4-dicyanebenzene (1,4-dcb). As a result of reaction between silver nitrate and 1,4-dcb we were able to isolate **4** in a repetitive manner, however not from all solvent mixtures. Silver nitrite did not react with the 1,4-dcb; from any applied solvents or mixtures of solvents such as acetone, THF, ethanol – toluene, acetone – toluene, water – acetonitrile we invariably obtained 1,4-dcb as the only crystalline product.

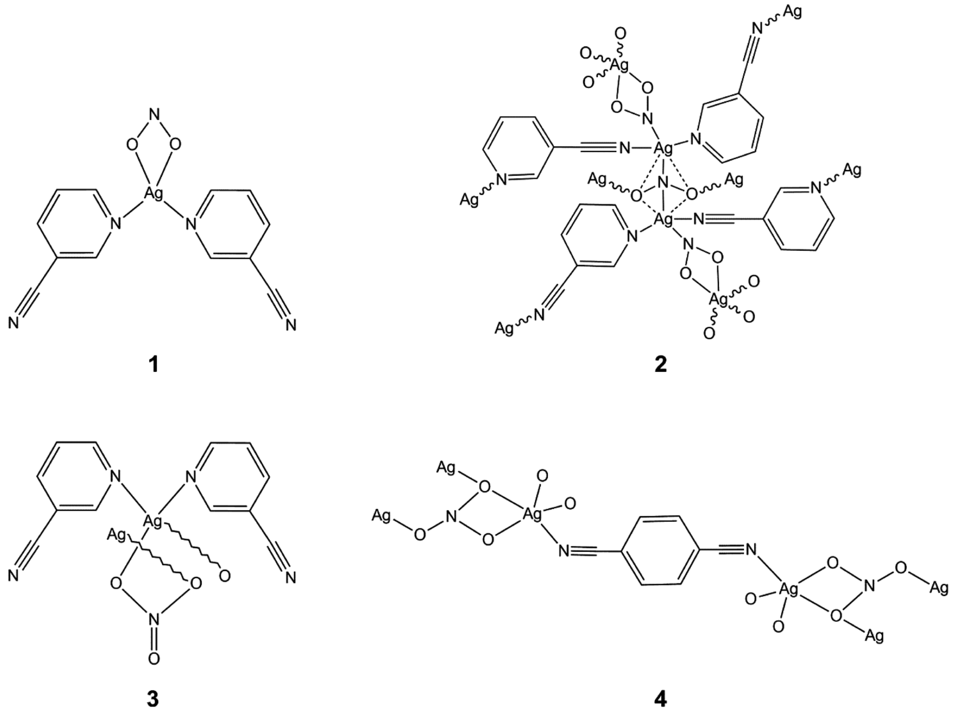
3.2. *Crystal structures*

In molecular compound **1** (Fig. 1) the coordination number of silver is formally equal to 4, with the doubly-coordinated nitrite. The geometry is far from any regular, *i.e.* tetrahedral or square planar for which geometrical indices τ_4/τ_4' are equal 0 or 1 respectively; for complex **1** $\tau_4 = 0.472$ [46] and $\tau_4' = 0.547$ [47], and the the coordination of nitrite is largely asymmetrical with one short Ag1—O1 equal to 2.343(2) Å) and one long Ag1—O2 bond or rather contact at 2.828(2) Å. Compound **1** can be also considered as a *quasi* trigonal complex of Ag(I) coordinated by nitrite and two molecules of 3-cyanopyridine and this interpretation is supported by the sum of angles around silver in such trigonal assembly with O1, N2 and N4 very close to 360° *i.e.* 358.6°. Certainly the individual angles around silver atom deviate strongly from 120° to fit additional out-of-plane interaction with the other oxygen of nitrite (Fig. 1 caption). If we calculate a plane defined by Ag1, N1, N2, and N4 than we see that all the atoms lie almost in the plane, with very small deviations not exceeding 0.019 Å, however the nitrite ion as well as cyanopyridine ligands are rotated with regard to this plane (Fig. 1S). The individual butterfly-like molecules pack in piles parallel to *a* axis. (Fig. 2S). The important bond lengths and angles are given in the Fig. 1 caption.

Complex **2**, which structure is demonstrated in Fig. 2a and b, is a 2-D coordination polymer. Both ligands: nitrite ion and 3-cyanopyridine serve as bridging units. The asymmetric unit (Fig. 2a) contains one and a half silver cation, one and a half nitrite anion accordingly as well as one bridging 3-cyanopyridine. The description of the structure of the polymer is further complicated by the fact that half occupied atoms/ions sit near the special positions and were modelled as disordered around them with equal occupancies – this is illustrated in Fig. 2b. The disorder involves Ag2 and the nitrite O3—N2—O4. Half-occupied Ag2 resides close to Wyckoff special position 1b in P-1, *i.e.* the atom is located close to the middle of the cell edge. Similarly, half-occupied NO_2^- sits in the vicinity of Wyckoff special position 1 g in P-1, which means that the nitrite ion is disordered over the center of the cell face. Such arrangement triggers either distorted tetrahedral coordination in which Ag1 is surrounded exclusively by atoms of nitrogen ($\tau_4 = 0.864$, $\tau_4' = 0.867$) or alternately distorted square pyramid AgN_3O_2 core ($\tau_5 = 0.181$). Interestingly the pyridine and nitrile nitrogen atoms involved in bonding with Ag1 show similar bond lengths Ag1—N3–2.341(2) Å and Ag1—N4–2.362(2) Å; we expected a larger difference with the longer nitrile Ag1—N4 bond and shorter pyridine Ag1—N3 interaction – the actual difference is only *ca.* 0.020 Å. The coordination geometry of Ag2 is closer to square planar ($\tau_4 = 0.260$, $\tau_4' = 0.259$) or square pyramid ($\tau_5 = 0.007$) with long Ag2—O3$^{\text{iv}}$/Ag2—O4$^{\text{vi}}$ contact of 2.642(9)/2.714(9) Å respectively. Atom Ag2 is coordinated exclusively by atoms of oxygen. The important bond lengths and angles are given in the Fig. 2 caption.

In the Fig. 3a the extended molecular structure of polymeric **2** is shown. The silver atoms are interconnected via nitrite anions within the layer and, at the same time, by 3-cyanopyridine molecules that close the silver nitrite system between them creating a 2-D CP. The additional aggregation in the third dimension results from the stacking π–π interactions of pyridine rings from the adjacent layers of the coordination polymer. These interactions are illustrated in Fig. 3b. Distances between the interacting rings are within the range 3.663–3.682 Å.

With the intention of comparing the silver nitrite and silver nitrate complexes we have also carried out the reaction of silver nitrate with 3-cpy. It is well known that nitrite has an especially large number of coordination modes as also illustrated by **1** and **2** and discussed in a number of both original and review papers *e.g.* [48,49]. Though, theoretically, coordination modes of nitrate is equally rich [50] nitrate ion can bind to metal ions exclusively via oxygen atoms and it is a much



Scheme 1. Formulas of the molecular complex **1** and coordination polymers **2**–**4**.

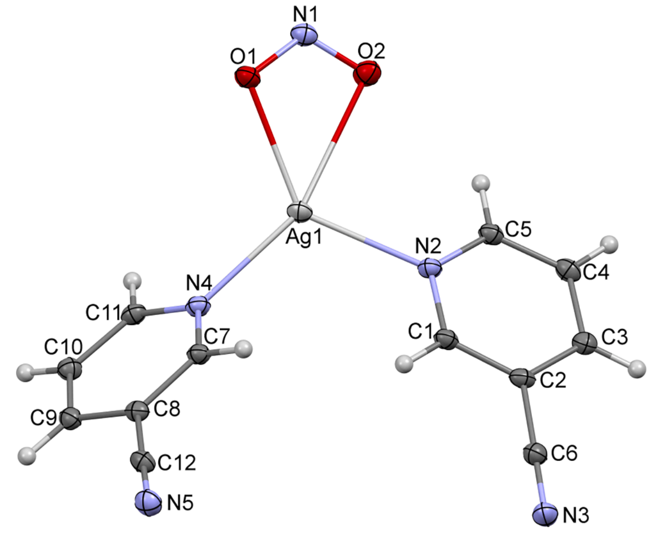


Fig. 1. Molecular structure of complex **1** with the numbering scheme. Important bond lengths [Å]: Ag1—O1 2.343(2), Ag1—O2 2.828(2), Ag1—N2, 2.302 (2), Ag1—N4 2.294(2). Important angles [°]: O1—Ag1—O2 49.93(7), N2—Ag1—N4 112.87(8), O1—Ag1—N2 134.60(8), O1—Ag1—N4 111.15(8), O2—Ag1—N2 88.12(8), O2—Ag1—N4 158.34(8).

weaker base than nitrite. Indeed in case of silver nitrate – 3-cpy system we observed the formation of only one coordination compound.

Complex **3** was first obtained by a slightly different method in 2004 [33]. It is a 1-D coordination polymer, at least in the solid state, with bridging nitrate and terminal 3-cyanopyridine, We present a 120 K redetermination data in Table 1 and molecular structure and data, altered due to low temperature measurement, in Fig. 4a and b and Fig. 4 caption. As expected the cell dimensions are slightly decreased and the bond lengths are determined with better accuracy than before. Long bond distances between Ag1 and O1 atoms in the system indicate large contribution of ionic interaction between the nitrate and $Ag(2\text{-}cpy)_2^+$ complex. This is also supported by the close-to-linear arrangement of 3-cpy ligands around Ag1 with N1—Ag1—N1^i equal to 156.8(4)° as well as by the crystal packing. The polarized chains with negatively and positively charged sides pack in a head-to-tail fashion as illustrated in Fig. 3S. We can additionally compare the bond lengths in **1**/**2** and **3** and see that the silver–pyridine nitrogen bonds are shorter in complex **3** whereas the distances between silver and oxygen are definitely longer in **3** than in **1** and **2** and the differences are substantial. The intrachain Ag···Ag separation of adjacent Ag atoms in a helical chain falls to 3.65 Å in 120 K, compared with the 3.72 Å described previously at RT [33], which is still longer than the van der Waals contact distance (3.40 Å). The closest interchain Ag···Ag contact is at 6.46 Å.

Complex **4** forms in a solution of silver(I) nitrate and 1,4-dcb; it crystallizes in $P2_1/c$ group of the monoclinic system. The structure of good quality crystals was solved to the very low discrepancy factor $R_1 = 0.0181$ ($R_{int} = 0.0244$). The asymmetric unit contains one silver atom, one nitrate(V) anion and half of the 1,4-dcb molecule. The silver ions feature C.N. = 5 in a distorted geometry and it is coordinated by three nitrates (one chelating) and one nitrile nitrogen of cyanobenzene. This molecular structure is illustrated in Fig. 5. Altogether the coordination pattern leads to 3-D polymer, which is depicted in Fig. 4S. The 3D net is penetrated by narrow channels with the flattened cross-section and the large and small diameters of 22 Å/4 Å (Fig. 4S).

3.3. FT-IR spectroscopy

The FT-IR ATR spectra of complexes **1**–**4** compared to their respective ligands and salts (silver nitrate/nitrite) are presented as the detailed Figs. 5S–7S of Supplementary content. Similar to many other known nitrile complexes the frequency of the band connected with the $\nu_{C\equiv N}$ stretch of the coordinated nitrile ligand in complexes **2** – **4** was increased in comparison to non-coordinated nitrile: as in 3-cpy or 1,4-dcb ligands or in complex **1** (Table 2). The analysis of the influence of σ- and π-bonding with the metal ion as well as the influence of the character of the group bonded to the nitrile on the IR modes can be found in the literature [51,52]. Though the shifts are typically not large (15 or 12 cm^{-1} in the case of **2** and **4**), the changes in the position of $\nu_{C\equiv N}$ are very

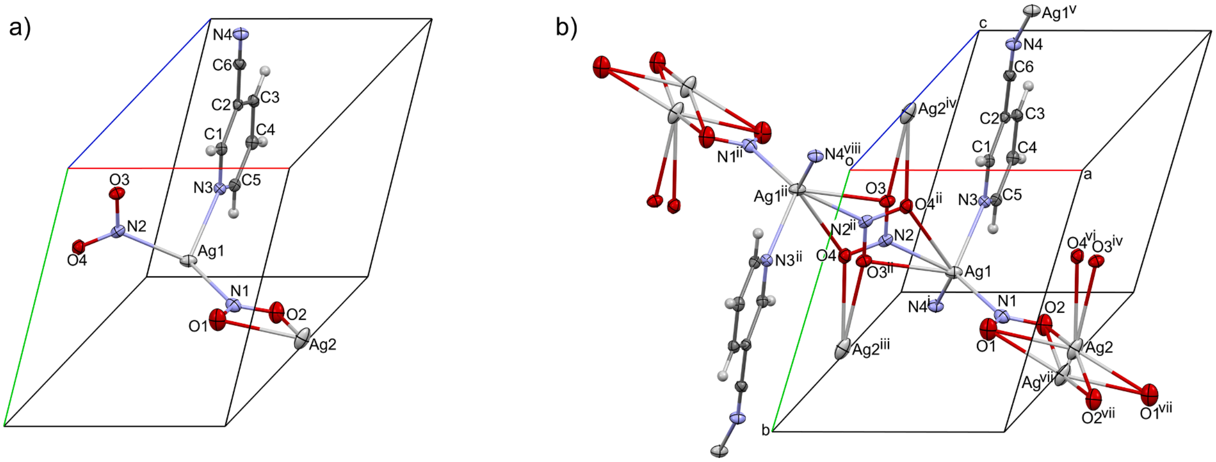


Fig. 2. Molecular structure of complex **2**, hydrogen atoms of pyridine ring removed for clarity, cell axes demonstrated: a) asymmetric unit with the numbering scheme and cell axes; b) fragment of the polymeric structure, both positions of the disordered Ag2 and nitrite O3—N2—O4 are shown. Important bond lengths [Å]: Ag1—N1, 2.255(2), Ag1—N2 2.235(5), Ag1—N3 2.3416(19), Ag1—N4^{i} 2.362(2), Ag1—O3^{ii} 2.551(7), Ag1—O4^{ii} 2.704(8), Ag2O1 2.523(2), Ag2—O2 2.324(2), Ag2—O1^{vii} 2.461(2), Ag2—O2^{vii} 2.475(2), Ag2—O3^{iv} 2.642(9), Ag2—O4^{vi} 2.714(9). Important angles [°]: N1—Ag1—N2 118.27(13), N2—Ag1—N3 97.81(14), N3—Ag1—N4^{i} 90.93(7), N1—Ag1—N3 119.49(8), N1—Ag1—N4^{i} 117.68(8), N2—Ag1—N4^{i} 107.99(16) O1—Ag2—O2 51.35(7), O1—Ag2—O2^{vii} 120.74(8), O2—Ag2—O1^{vii} 130.42(8), O1—Ag2—O1^{vii} 161.68(3), O2—Ag2—O2^{vii} 161.26(3). Symmetry operations: ^{i} = x, 1 + y, z; ^{ii} = −x, 1 − y, 1 − z; ^{iii} = −1 + x, y, z; ^{iv} = 1 − x, 1 − y, 1 − z; ^{v} = x, −1 + y, z; ^{vi} = 1 + x, y, z; ^{vii} = 2 − x, 2 − y, 1 − z.

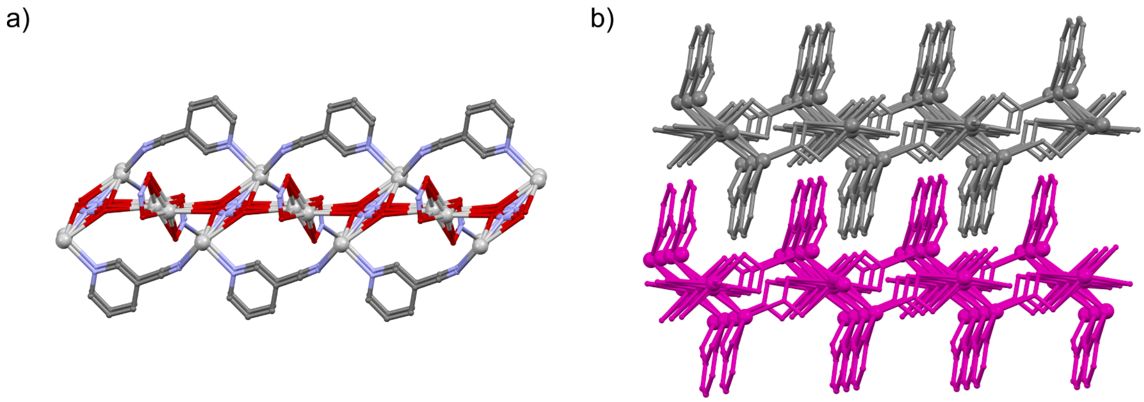


Fig. 3. Crystal packing of **3**, hydrogen atoms of pyridine ring removed for clarity: a) structure of a single layer b) interlayer stacking interactions.

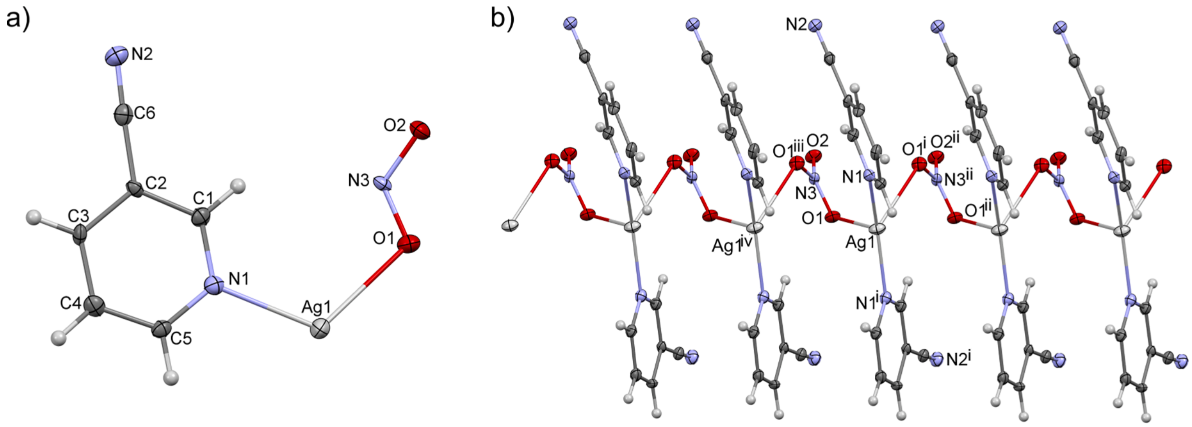


Fig. 4. Molecular structure of complex **3**: a) asymmetric unit with the numbering scheme; b) fragment of the polymeric structure. Important bond lengths [Å]: Ag1—N1, 2.222(3), Ag1—O1, 2.678(6), Ag1···Ag1^{iv} 3.6513(4), Important angles [°]: N1—Ag1—N1^{i} 156.8(4), N1—Ag1—O1 116.0(2), N1—Ag1—O1^{i} 83.4(2), O1—Ag1—O1^{i} 72.4(3). Symmetry operations: ^{i} = 3 − x, y, 2-z; ^{ii} = x, y, 1 + z; ^{iii} = 3 − x, y, 1 − z; ^{iv} = x, y, −1 + z.

useful for the identification of the type of nitrile coordination. This usefulness is due to the specific position of the nitrile stretching mode on the frequency scale, which can be well-resolved even in the presence of water [53].

On the other hand in the IR spectra we can observe distinct modes for the different coordination of nitrite in **1** and **2** and nitrate in **3** and **4**. We

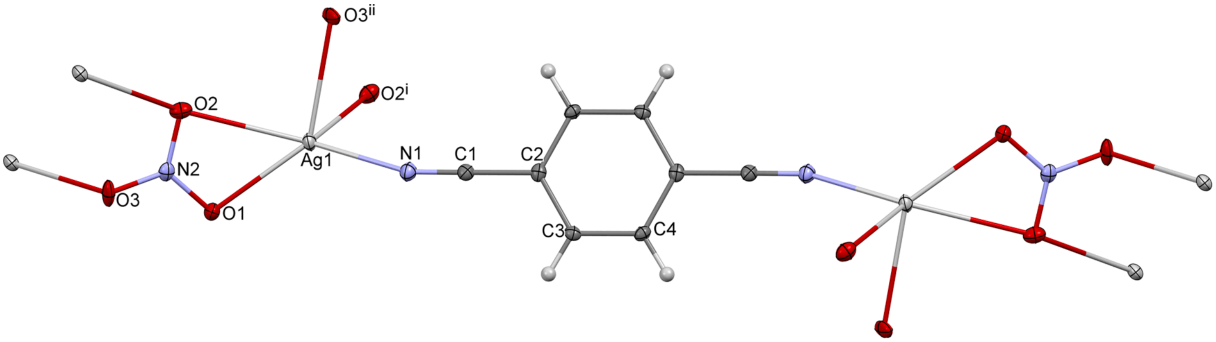


Fig. 5. Molecular structure of complex **4** with the numbering scheme for the independent part and the atoms in the coordination sphere of Ag1. Important bond lengths [Å]: Ag1—N1, 2.256(2), Ag1—O1, 2.3775(18), Ag1—O2, 2.655(2), Ag1—O2^{i}, 2.580(2), Ag1—O3, 2.5647(19). Important angles [°]:N1—Ag1—O1 125.69 (7), N1—Ag1—O2 146.37(7), N1—Ag1—O2^{i} 91.98(7), N1—Ag1—O3^{ii} 91.88(8), O1—Ag1—O2^{i} 122.39(6), O1—Ag1—O3^{ii} 135.45(6). Symmetry operations: ^{i} = x, ½—y, −½ + z; ^{ii} = −1 + x, ½—y, −½ + z.

Table 2
The frequencies of the $\nu_{C\equiv N}$ stretching mode in 3-cpy, 1,4-dcb and complexes **1**–**4**.

Compd.	$\nu_{C\equiv N}$ [cm^{-1}]	$\Delta\nu_{C\equiv N}$ [cm^{-1}] vs. non-coordinated ligand	Comment
3-cpy	2230	–	
1	2235	+5	Non-coordinated nitrile
2	2245	+15	Coordinated nitrile
3	2233	+3	Non-coordinated nitrile
1,4-dcb	2232	–	
4	2244	+12	Coordinated nitrile

Table 3
The excitation and emission maxima for studied compounds.

Compound	Excitation, λ_{max} [nm]	Emission, λ_{max} [nm]
3-cpy	329.0	369.0
1.4-dcb	294.0	355.8
1	375.0	415.8
2	340.0	409.2 549.8 569.4
4	297.0	366.8

can undoubtedly identify one of the two $\nu_{N=O}$ stretching modes of (chelating) nitrito complex **1** at 1160 cm^{-1} and δ_{ONO} at 825 cm^{-1}. The remaining bands overlap with the 3-cpy modes. In the spectrum of **2**, which is more complex we could identify two different locations of $\nu_{aN=O}$ stretching modes at 1250 and 1238 cm^{-1} and δ_{ONO} at 845 cm^{-1}. The $\nu_{N=O}$ stretching modes are better resolved in the spectra of complexes **1** and **2** compared with the spectrum of silver nitrite [53].

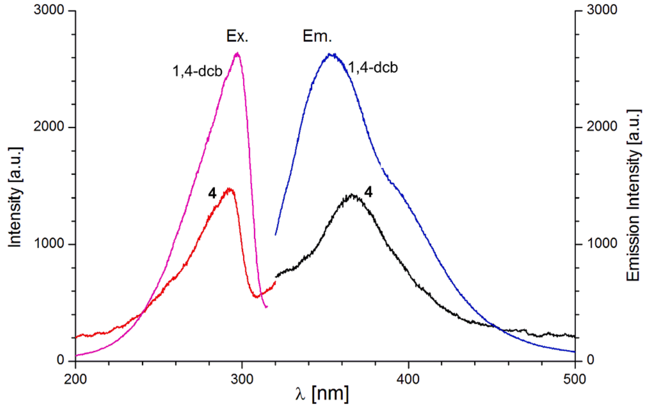


Fig. 6. Solid state emission and excitation spectra of **4** and free 1,4-dcb ligand at RT. Complex **4**: red line - excitation spectrum at λ_{ob} = 367 nm, black line – emission spectrum at λ_{ex} = 297 nm. Ligand 1,4-dicyanobenzene (1,4-dcb): magenta line – excitation spectrum at λ_{ob} = 356 nm, blue line – emission spectrum at λ_{ex} = 294 nm. Slits 2.5/1 nm.

The strongest band out of three possible stretching modes of nitrate was shifted to 1317 cm^{-1} (compared to 1293 cm^{-1} of silver nitrate) in complex **3** (Fig. 6S) and split to 1298/1297 cm^{-1} in complex **4** (Fig. 7S) [53].

3.4. *Luminescent properties*

The photoluminescence spectra of compounds **1**–**4** as well as the free 3-cpy and 1,4-dcb ligands in solid state at room temperature are shown in Figs. 6 and 7 and Figs. 8S and 9S. All excitation and local emission maxima are summarized in Table 3. The 3-cpy ligand exhibits a strong luminescent band at 369.0 nm upon excitation at 329.0 nm (Fig. 8S). Ligand 1,4-dcb shows a main emission peak at 355.8 nm under the excitation of 294.0 nm light (Fig. 6). The emission peaks of these ligands are much stronger than that of complexes **1**, **2** and **4**. The compounds **1** and **2** exhibit blue emissions at 298 K. The main emission peak for **1** is located at 415.8 nm (λ_{ex} = 375 nm, Fig. 9S). Upon excitation at λ_{ex} = 340 nm, the emission spectrum for the compound **2** shows three peaks at λ = 409.2 nm, 549.8 and 569.4 nm (Fig. 7). The emission maxima for **1**–**2** are red-shifted in comparison to the location of maximum luminescence of 3-cpy ligand (λ_{em} = 369.0 nm). Compound **4** displays one band at λ_{em} = 366,8 nm. The emission spectrum of **4** shows a similar shape and maximum to that of free 1,4-dcb ligand (Fig. 6). The similarity in the emission and excitation spectra of 1,4-dcb and **4** suggests that the

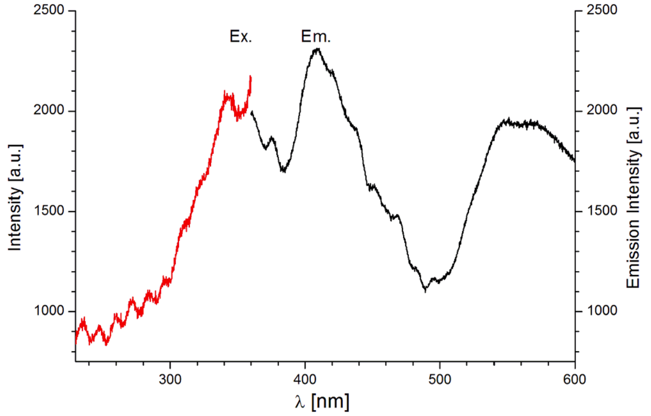


Fig. 7. Emission and excitation spectra of **2** in solid state; red line - excitation spectrum at λ_{ob} = 409 nm, black line – emission spectrum at λ_{ex} = 340 nm, slits 5/5 nm. ((Colour online.))

luminescence of the **4** is a result of a ligand based absorption [54,55]. Compared with the 1,4-dcb, **4** exhibits red shift of 11 nm. The emission spectral peaks at 415.8 nm for **1** and 409.2 nm for **2** are assigned to π–π* transitions of 3-cyanopyridine ligand while the additional two maxima at 549,8 and 569,4 nm may be attributed to LMCT or MLCT, caused by Ag-N containing chromophores [56,57]. The differences in the emission spectra of **1** and **2** must be certainly attributed to their different structures as the ligands are the same [36,58]. Compound **2** showed a weaker emission compared with **1**, which indicates that the emission is rather quenched than enhanced by the formation of the extended network of the polymer. However, the presence of additional, distinct emission bands in the visible region confirms the formation of additional metal–ligand bonds and energy levels within the system together with the new possible mechanisms of fluorophore relaxation (Fig. 7).

Among the studied compounds complex **4** is the strongest emitter, with the emission related to the presence of 1,4-dcb ligand.

4. Conclusions

Relatively simple system of weak nitrile ligands and silver nitrite/nitrate allowed the formation and isolation of coordination compounds of diverse nuclearity and dimensionality. Both nitrite and nitrate form polydimensional complexes, however long bond distances between Ag and O atoms within the nitrate complexes indicate larger contribution of ionic interaction between the nitrate and metal ion compared to nitrite compounds. The extension of the network does not enhance the luminescent properties of the ligands in the studied complexes, however in complex **2** it gives rise to the new LMCT or MLCT bands in the visible region. Among the studied compounds the complex **4** is the strongest emitter and may be considered a candidate for potential hybrid inorganic–organic photoactive material.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2022.115831.

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