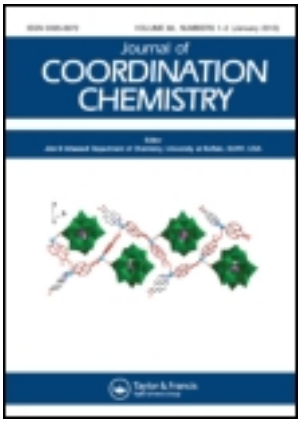

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Silver(I) coordination polymer and nine-coordinated cadmium(II) complex with dimethyl pyridine-2,6-dicarboxylate supported by solid state and electrochemical studies

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Silver(I) coordination polymer and nine-coordinated cadmium(II) complex with dimethyl pyridine-2,6-dicarboxylate supported by solid state and electrochemical studies

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Two complexes of dimethyl pyridine-2,6-dicarboxylate (L), $[CdL_3][CdI_4]$ (**1**) and $[Ag(L)NO_3]_n$ (**2**) were prepared and identified by elemental analysis, FT-IR, Raman and ^{1}H NMR spectroscopy, cyclic voltammetry, and single-crystal X-ray diffraction. The crystal structure of **1** contains both complex cation and complex anion of the metal. Cadmium in $[CdL_3]^{2+}$, coordinated by three nitrogens and six oxygens, has a distorted tricapped trigonal prismatic geometry while $[CdI_4]^{2-}$, with four coordinated iodides, has a slightly distorted tetrahedral geometry. In the crystal structure of **2,** silver has distorted tetrahedral geometry by coordination of nitrogen and three oxygens. One oxygen of nitrate in **2** bridges two silvers. Extension of these bridges forms a 1-D coordination polymer. Cyclic voltammetry of L reveals two reduction steps which are shifted after coordination in **1,** while no significant shifts are observed in **2**. Hydrogen bonds including C–H···I, C–H···O and C–H···C and short interactions such as C···I, $\pi \cdots \pi$, and $\pi \cdots$O are compared with Cambridge Structural Database analogs. Two brief structural surveys on ligand coordination modes and silver polymers are also presented.

Keywords: Dimethyl pyridine-2; 6-dicarboxylate; Silver(I) coordination polymer; Cadmium iodide; Cyclic voltammetry; X-ray crystal structure

1. Introduction

Coordination polymers are of interest [1] and a variety of silver(I) coordination polymers with nitrogen- [2] or oxygen donors [3] or combination with both [4] provide information on supramolecular isomerism. These polymers have properties such as photoluminescence, magnetism, conductivity and pharmaceuticals [5–8]. Coordination architectures depend mainly on two factors, coordination geometry of the metal ions and the nature of the ligands [9]. Silver has diverse coordination geometry with coordination numbers in the

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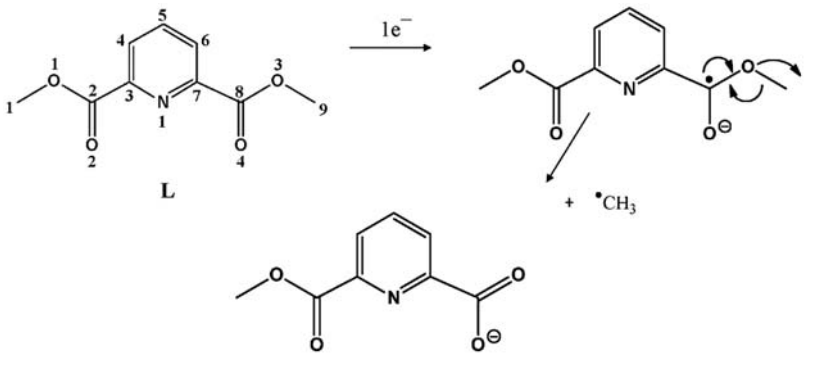


Scheme 1. L, numbering scheme used for the ^{1}H NMR spectra assignments. In this scheme, the proposed mechanism for reduction of L is shown.

Cambridge Structural Database (CSD) [10] varying from one [11], two [12], three [13], four [14], five [15], six [16], seven [17], eight [18], nine [19], ten [20], eleven [21], and twelve [22]. Coordination number of four is common. Silver-ligand bonds are usually weak and, therefore, various noncovalent bonds (hydrogen, π–π stacking, etc.) can exert greater effect on the structures formed than in stronger metal-ligand systems [23].

In this work, preparation and characterization of d^{10} configuration metals (Cd, Ag) with dimethyl pyridine-2,6-dicarboxylate (L, scheme 1), $[CdL_3][CdI_4]$ (**1**) and $[Ag(L)NO_3]_n$ (**2**) are described. Similar structures with the analogous dipicolinic acid have been reported [24, 25]. A search of the CSD database on complexes of dipicolinic acid revealed mononuclear [26], binuclear [27] and polymeric [28] structures with cadmium and also mononuclear [29] and polymeric [30] structures with silver.

Study of the CSD database by ConQuest [31] revealed that cadmium has different coordination numbers, two [32], three [33], four [34], five [35], six [36], seven [37], eight [38], nine [39], and ten [40]. In this paper, we introduce coordination of L with cadmium and silver.

2. Experimental

2.1. *Instrumentation and reagents*

All chemicals and solvents were reagent or analytical grade and used as received. L was prepared accordingly to the literature [41]. A conventional three-electrode system was employed for voltammetry with a PGSTAT101 and glassy carbon working electrode. Carbon, hydrogen, and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. Infrared spectra as KBr pellets were recorded from 400–4000 cm^{-1} using a FT–IR 8400-Shimadzu spectrometer. Raman spectrum was obtained using a Nicolet Model 910 FT spectrometer. Melting points were determined using a Barnsted Electrothermal 9200 electrically heated apparatus. ^{1}H NMR spectra were recorded on a Bruker Aspect 3000 instrument operating at 250 MHz; chemical shifts are given in parts per million with values referenced to an internal standard of Tetramethylsilane.

2.2. *Synthesis*

2.2.1. Synthesis of $[CdL_3][CdI_4]$ (1). CdI_2 (1 mM, 0.36 g) was dissolved in EtOH (10 mL) and added with stirring to a solution of L (2 mM, 0.38 g) in EtOH (5 mL). A white precipitate formed immediately. After 3 h, the precipitate was filtered, and the resulting solution was left at room temperature. Colorless crystals suitable for X-ray diffraction were obtained after several days. The melting point, CHN analysis, and IR spectroscopy of the crystals were identical to those of the initial precipitate. m.p. 168 °C. Anal. Calcd for $C_{27}H_{27}Cd_2I_4N_3O_{12}$ (%): C, 24.61; H, 2.06; N, 3.19. Found: C, 24.63; H, 2.06; N, 3.11. IR (KBr, cm^{-1}): 3070 w (ν CH_{ar}), 2951 w (ν CH), 1728 *versus* (ν C=O), 1589 m (ν C=N), 1435 m (δ_{as} CH_3), 1315 s (δ_s CH_3 and/or ν C−O), 1265 s (ν C−O), 756 s and 694 m (γ py). Raman (cm^{-1}): 1498 *versus* (ν C=C), 1358 m, 1249 s (ν C−O), 724 w and 635 *versus* (γ py), 509 m (ν Cd–N), 264 w (ν Cd–O), 100 s (ν Cd–I). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.90$ (s, C^1H_3, C^9H_3, 6H), 8.17−8.27 (m, C^5H, C^4H, C^6H, 3H) ppm. Cyclic voltammetry (glassy carbon, 50 mV s^{-1} scan rate): E(L/L^{-1}) −1.82 V, E(L^{-1}/L^{-2}) −2.23 V *versus* Ag/AgCl.

2.2.2. Synthesis of $[Ag(L)NO_3]_n$ (2). $AgNO_3$ (1 mM, 0.17 g) was suspended in EtOH (20 mL) and added with stirring to a solution of L (1 mM, 0.19 g) in EtOH (10 mL). After 1 min, the reaction mixture was clear and stirring was continued for 2 h at 60 °C. Colorless crystals suitable for X-ray diffraction were obtained from the solution after a day. Yield: 0.32 g, 89%; m.p. 160 °C. Anal. Calcd for $C_9H_9AgN_2O_7$ (%): C, 29.61; H, 2.49; N, 7.67.

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{27}H_{27}Cd_2I_4N_3O_{12}$	$C_9H_9N_2O_7Ag$
Formula weight (gM^{-1})	1317.91	365.05
Temperature (K)	150	150
Crystal system	Trigonal	Monoclinic
Space group	*R*3	$P2_1/c$
Unit cell dimensions (Å, °)		
a	12.3621(13)	9.9713(4)
b	12.3621(13)	15.4651(6)
c	22.403(2)	7.6495(3)
α	90.00	90.00
β	90.00	95.029(4)
γ	120.00	90.00
Volume ($Å^3$), *Z*	2964.9(5), 3	1175.06(8), 4
Calculated density (mg mm^{-3})	2.214	2.063
Absorption coefficient (mm^{-1})	4.255	1.748
F(000)	1842	720
Crystal size (mm^3)	0.06 × 0.06 × 0.02	0.17 × 0.03 × 0.02
2θ range for data collection (°)	6.6–58.06	5.96–58.76
h, *k*, *l* ranges	−16 : 16, −16 : 15, −30 : 15	−13 : 13, −19 : 20, −9 : 10
Reflections collected	2415	5640
Independent reflections	1698	2687
R_{int}	0.0234	0.0220
Data/restraints/parameters	1698/1/147	2687/0/174
Goodness-of-fit on F^2	1.096	1.047
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0280$, $wR_2 = 0.0566$	$R_1 = 0.0248$, $wR_2 = 0.0498$
R indices (all data)	$R_1 = 0.0302$, $wR_2 = 0.0588$	$R_1 = 0.0322$, $wR_2 = 0.0530$
Largest diff. peak and hole ($e.Å^{-3}$)	0.670 and −0.569	0.397 and −0.324

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Bond lengths (Å)			
Cd(1)–O(1)	2.568(5)	Ag(1)–N(1)	2.302(2)
Cd(1)–O(3)	2.548(6)	Ag(1)–O(4)	2.605(2)
Cd(1)–N(1)	2.33(1)	Ag(1)–O(5)	2.686(2)
Cd(2)–I(1)	2.7764(7)	Ag(1)–O(5)	2.315(2)
Cd(2)–I(2)	2.790(1)	N(2)–O(5)	1.283(3)
		N(2)–O(6)	1.238(3)
		N(2)–O(7)	1.240(3)
Angles (°)			
O(1)–Cd(1)–N(1)	67.3(2)	N(1)–Ag(1)–O(4)	68.84(6)
O(3)–Cd(1)–N(1)	68.1(2)	O(5)–Ag(1)–O(5)	99.78(5)
I(1)–Cd(1)–I(1)	110.81(4)	N(2)–O(5)–Ag(1)	97.3(1)
I(1)–Cd(1)–I(2)	108.08(4)	O(5)–N(2)–O(6)	119.0(2)
		O(6)–N(2)–O(7)	122.1(2)
		O(7)–N(2)–O(5)	118.9(2)

Found: C, 29.55; H, 2.48; N, 7.72. IR (KBr, cm^{-1}): 3016 w (ν CH_{ar}), 2966 w (ν CH), 1743 *versus* (ν C=O), 1574 m (ν C=N), 1439 m (δ_{as} CH_3), 1381 *versus* (ν_4 NO_3), 1292 s (ν_1 NO_3 and/or ν C−O), 1246 *versus* (ν C−O), 1084 w (ν_2 NO_3), 814 w (ν_6 NO_3), 756 m and 694 m (γ py). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.91$ (s, C^1H_3, C^9H_3, 6H), 8.19−8.31 (m, C^5H, C^4H, C^6H, 3H) ppm. Cyclic voltammetry (glassy carbon, 50 mV s^{-1} scan rate): E(L/L^{-1}) −1.77 V, E(L^{-1}/L^{-2}) −2.01 V *versus* Ag/AgCl.

2.3. *Crystal structure determination and refinement*

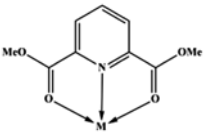
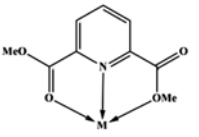
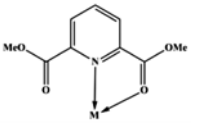
Suitable crystals of **1** and **2** were placed on an Oxford Diffraction Gemini Ultra and a Xcalibur Eos Gemini Ultra diffractometers, respectively, and kept at 150.0 K during data collection. Using OLEX-2 [42], the structures were solved with the SHELXS [43] structure solution program using direct methods and refined with the SHELXL [43] refinement package using least squares minimization. Diagrams of the molecular structures and unit cells were created using ORTEP-3 [44], Mercury (*version 3.0*) [45] and Diamond (*version 3.2g*) [46] softwares. Table 1 contains crystallographic data and details of the data collection and structure refinement. Selected bond lengths (Å) and angles (°) for **1** and **2** are listed in table 2.

3. Results and discussion

3.1. *Spectroscopic and electrochemical characterization*

Dimethyl pyridine-2,6-dicarboxylate has previously been synthesized and characterized by Alcock *et al*. [41]. Its cyclic voltammetry data are reported in this work. A search of the CSD database revealed that only three complexes of L have previously been reported. All coordination modes of L were extracted and presented in table 3. Among these modes, the bichelate-α and monochelate modes were observed in **1** and **2**, respectively. Reactions

Table 3. Different types of coordination for L.

Coordination modes for L			
Name	Bichelate-α mode	Bichelate-β mode	Monochelate mode
Coordinated metal ions	Cu^{2+}	Cu^{2+}	Cu^{+}
References	[55]	[55]	[56]

between dimethyl pyridine-2,6-dicarboxylate and ethanolic solution of cadmium(II) iodide and silver(I) nitrate in molar ratios of 1 : 2 and 1 : 1 (M : L), respectively, provided colorless crystals of **1** and **2**. These complexes were characterized by IR, Raman and ^{1}H NMR spectroscopy, cyclic voltammetry and X-ray crystallography. These complexes are air-stable and soluble in Dimethylsulfoxide (DMSO) and Dimethylformamide.

In IR spectra of **1**, **2** and L, there is a band above 1700 cm^{-1} assigned to ν (C=O). The ν (C=O) in the IR spectrum of **1** shifts 18 cm^{-1} to lower energy, indicating coordination through the carbonyl oxygen. No shift was observed for ν (C=O) in **2**. Four bands in the IR spectrum of **2** near 1381, 1292, 1084, and 814 cm^{-1} can be assigned to coordinated nitrate (respectively the vibrations ν_4, ν_1, ν_2 and ν_6). The difference between the ν_4 and the ν_1 positions is 89 cm^{-1}, typical for monodentate nitrate (bidentate nitrate displays a much bigger splitting) [47, 48]. In the IR spectrum of **2** the ν_1 (NO_3) overlapped with vibration due to ν (C–O).

In the Raman spectrum of **1**, ν (C=N) and ν (C=O) were not observed. The Cd–N and Cd–O stretches were assigned to bands at 509 and 264 cm^{-1}, respectively, consistent with values reported [49]. Four terminal Cd–I stretching vibrations were assigned to the strong band at 100 cm^{-1}. Similar results were reported previously [50].

The numbering scheme used for ^{1}H NMR spectrum of the free ligand is given in Scheme 1. In the ^{1}H NMR spectra of **1**, **2** and L, there are two groups of signals near 4 and above 8 ppm. The singlet at 4 ppm is assigned to OCH_3 and the multiplet at 8 ppm is assigned to protons of pyridine.

Only a few studies that deal with reduction of esters at electrode surfaces have been published. In general, it has been accepted that the electrode reaction mechanism involves an electron transfer, and the radical anion that is produced undergoes dissociation in a second and distinct step [51]. The one electron reduction of L produces a methyl radical and the stable anionic form of the ester from cleavage of one O–R bond (figure 1). After the first electron reduction step, the extra negative charge is situated on the molecule. This is likely to raise the activation energy required to add another electron or increase the free energy of the final product so as to make further reduction more difficult [52]. The cyclic voltammetry for **1**, **2,** and L were performed from −3 to + 1.6 V in DMSO solution containing 0.10 M Tetrabutylammonium perchlorate. The cyclic voltammograms of L and overlapped cyclic voltammograms of **1** and **2** with L are shown in Supplementary Material. The cyclic voltammogram of L shows two irreversible waves at –1.75 and –2.03 V corresponding to L/L^{-1} and L^{-1}/L^{-2}, respectively. These waves in the cadmium complex shift to lower voltage, indicating that after coordination, reduction of ligand becomes more difficult. This is reasonable because in reduction the oxygen of carbonyl, which accepts

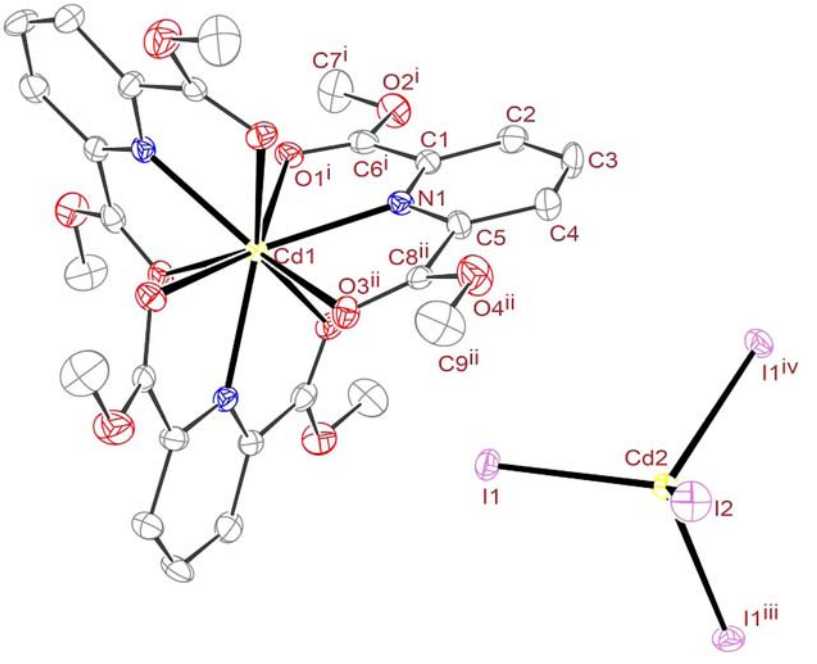


Figure 1. The ORTEP-3 diagram of the molecular structure of **1**. The ellipsoid for **1** is drawn at 30% probability level. Hydrogens were omitted for clarity.

the electron and starts the cleavage process, was coordinated to cadmium. The shifts in silver(I) complex are negligible, attributed to weak interaction between ligand and silver.

3.2. *Description of the crystal structures*

In the crystal structure of **1** (figure 1), there are two cadmiums with different geometries. Cd1 with coordination number nine has a distorted tricapped trigonal prismatic coordination environment (figure 2). Six sites are occupied by oxygens of the carbonyl groups with Cd–O bond lengths 2.548(6)–2.569(6) Å. The bond lengths are longer than those of CSD average (2.400 Å). The three other sites are occupied by pyridine nitrogens. Comparing Cd–N bond lengths (table 2) with average in the CSD revealed that Cd–N is comparable (2.333 Å). Cd2 has a different environment with slightly distorted tetrahedral geometry. A search of the CSD database revealed that coordination number of cadmium and average Cd−I bond lengths in complexes containing solely iodides is four and 2.792 Å, respectively (similarly in **1**). Three ligands are tridentate forming six five-membered chelate rings with Cd1. With respect to the pyridine ring planes in **1**, one carbonyl is above the plane, while the other is below, thus L is not planar. We also considered the crystal structure of L [53] and observed a similar result. If the distortion in the $[CdL_3]^{2+}$ unit is disregarded with a C_3 axis and three perpendicular C_2 axes to the C_3 axis it has D_3 symmetry (figure 3).

In the crystal network of **1** (figure 4), there are intermolecular C–Hπ, C–H$\cdots$I hydrogen bonds (table 4) and C$\cdots$I interactions (table 5). The hydrogen bonds were compared with analogs in table 4. Each $[CdL_3]^{2+}$ unit was surrounded by six $[CdI_4]^{2-}$ units and vice

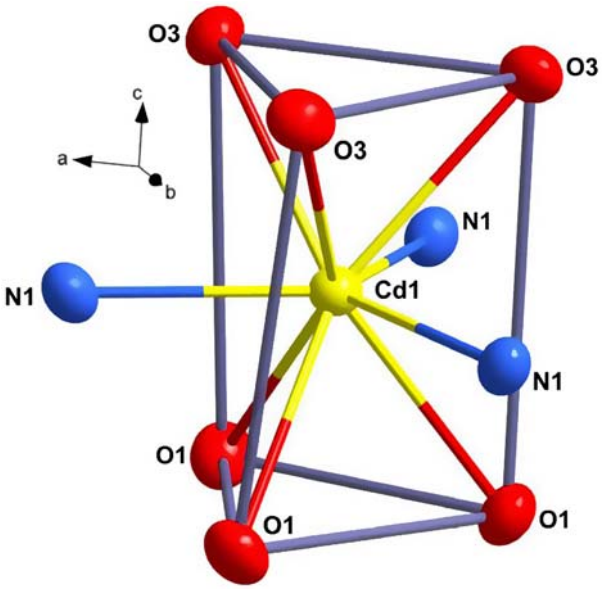


Figure 2. Distorted tricapped trigonal prismatic geometry around the Cd1 in **1**.

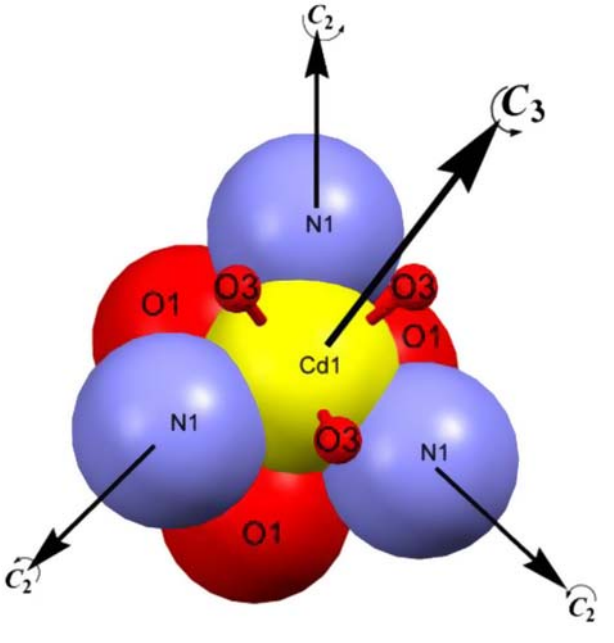


Figure 3. D_3 symmetry of $[CdL_3]^{2+}$ unit in **1**.

versa (figure 4). The distance average for C···I interactions in the CSD is 3.583 Å, comparable with the interactions in **1**.

In the crystal structure of **2**, silver, coordinated by two oxygens of nitrates, one oxygen and nitrogen of L has a distorted tetrahedral geometry (figure 5). In the solid, O5 of nitrate

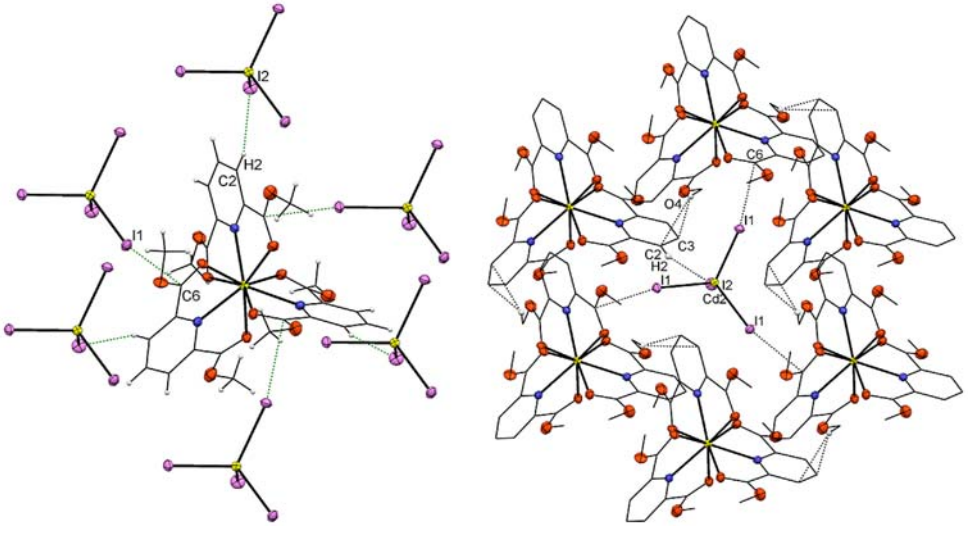


Figure 4. Packing of **1**. Each $[CdL_3]^{2+}$ is surrounded by six $[CdI_4]^{2-}$ units and vice versa. Some interactions including C···I and C–H···π are presented. Only hydrogens involved in hydrogen bonding are shown.

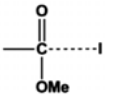
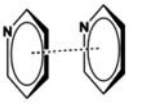
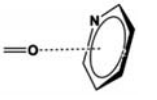
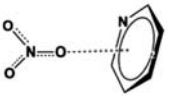
Table 4. Dimensions of the hydrogen bonds (Å and °) in **1** and **2**. CSD average for each interaction and the base which was searched.

	D–H···A	*d*(D–H)	*d*(H···A)	∠(DHA)	*d*(D···A)	CSD average for *d*(H···A)	Searched base in the CSD
1							
	C(2)–H(2)···I(2)#1	0.93	2.9950	160.8	3.88(1)	3.092	
	C(9)–H(9C)···π	0.96	2.82	144.4	3.65(2)	2.805	
2							
	C(1)–H(1C)···O(7)#3	0.980	2.521	156.9	3.443(4)	2.573	
	C(5)–H(5)···O(5)#4	0.950	2.397	156.0	3.288(3)	2.563	
	C(6)–H(6)···O(2)#5	0.950	2.660	136.5	3.413(3)	2.531	
	C(9)–H(9B)···O(6)#6	0.981	2.468	164.7	3.424(4)	2.573	

Symmetry transformations used to generate equivalent atoms: #1 −2/3+x, 2/3+y, −1/3+z; #2 2/3−x+y, 4/3−x, 1/3+z; #3 1+x, 1.5−y, −0.5+z; #4 x, 1.5−y, −0.5+z; #5 2−x, −0.5+y, 1.5−z; #6 1−x, −0.5+y, 1.5−z.

forms a bridge between two adjacent silvers. Expansion of the bridges in the *c* direction produces a 1-D coordination polymer (figure 6). We compared all coordinated bond lengths with CSD averages. The comparison revealed that the Ag–O_L (2.605(2) Å) and

Table 5. Dimension of the short contacts (Å) in **1** and **2**. CSD average for each interaction and the base which was searched.

	Interactions	*d*	CSD average for *d*	Searched base in the CSD
1	C(6)···I(1)	3.629(8)	3.583	
2	$\pi\cdots\pi$	3.336(3)	3.326	
	$\pi\cdots$O(4)	3.192(3)	3.144	
	$\pi\cdots$O(5)	3.114(3)	3.150	

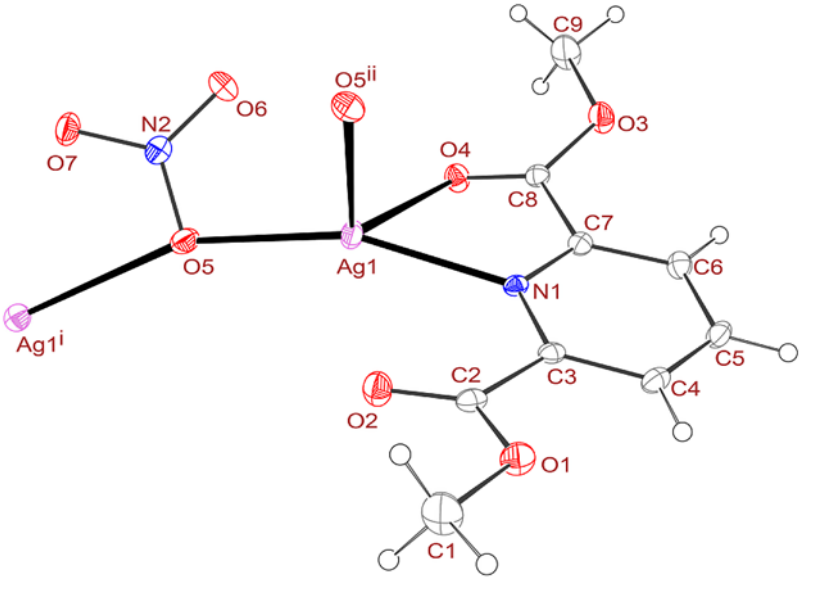


Figure 5. The ORTEP-3 diagram of the molecular structure of **2**. The ellipsoid for **2** is drawn at 40% probability level.

Ag–N_L (2.302(2) Å) are longer than the CSD averages (2.531 and 2.253 Å for Ag–O and Ag–N, respectively). The Ag–$O_{nitrate}$ bond length average (2.5005 Å) in **2** is similar to the CSD average (2.5245 Å).

We have studied all silver(I) polymers in the CSD database for Scheme 2 parameters and the results are listed in table 6. With replacement of X from small to large halides the Ag–X bond length increases while the ANG value decreases.

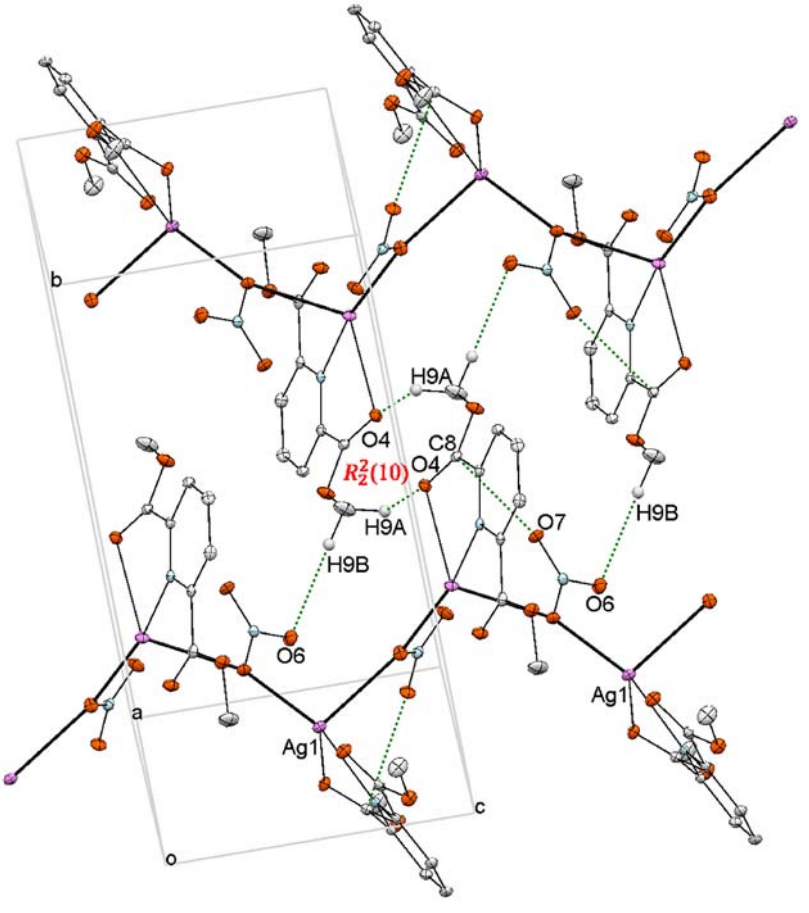
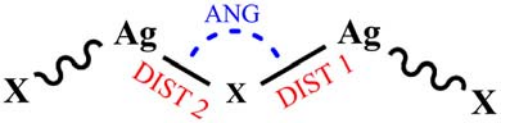


Figure 6. Nitrate bridge expansion in the *c* direction producing 1D silver(I) coordination polymer. Two C(9)–H(9A)···O(4) hydrogen bonds form a $R_2^2(10)$ motif. The polymeric chain is shown with bold lines.

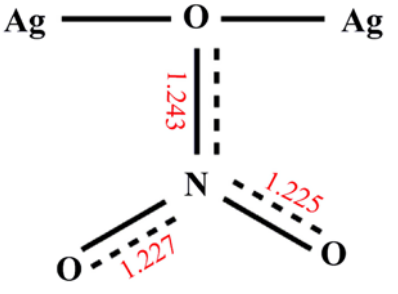


Scheme 2. The base which was searched for silver(I) polymers in the CSD database.

The average of N–O bond lengths between all silver(I) polymers containing nitrate bridges in the CSD were calculated by Vista [54] and the results are presented in Scheme 3. NO_{bridge} is longer than the others as observed in **2**. Each nitrate has six interactions with adjacent molecules, listed in tables 4 and 5, and compared with CSD analogs. In the unit cell of **2**, two C(9)–H(9A)···O(4) hydrogen bonds participate in formation of a $R_2{}^2(10)$ motif between two ester arms belonging to different ligands in adjacent chains (figure 6).

Table 6. Results of the survey on the CSD database for silver(I) polymers based on scheme 2.

X	DIST (DIST 1 and 2 average, Å)	ANG (°)	X	DIST (DIST 1 and 2 average, Å)	ANG (°)
C	2.454	109.497	O	2.449	97.99
N	2.1675	92.136	S	2.594	98.541
			Se	2.708	90.402
F	2.496	114.332	Ag	3.148	86.813
Cl	2.709	104.276	Sn	2.938	57.296
Br	2.781	90.725	Te	2.886	74.347
I	2.900	86.406	W	2.951	94.099



Scheme 3. CSD averages for the three N–O bond lengths of nitrate in all silver polymers containing nitrate bridge.

4. Conclusion

$[CdL_3][CdI_4]$ (**1**) and $[Ag(L)NO_3]_n$ (**2**) were synthesized in reaction between cadmium(II) iodide and silver(I) nitrate with L (dimethyl pyridine-2,6-dicarboxylate). For these complexes, spectral (IR, Raman, ^{1}H NMR), electrochemical, and structural properties were investigated. Complex **1** exhibits two cadmiums with different geometries, distorted tricapped trigonal prismatic and slightly distorted tetrahedral. Complex **2** has distorted tetrahedral geometry for silver; the oxygen of nitrate forms a bridge between two adjacent silvers and produces a 1D silver(I) coordination polymer. A survey on cadmium and silver complexes reveals that cadmium and silver have coordination numbers from 2 to 10 and 1 to 12, respectively. Another survey on complexes of L showed that this ligand has three coordination modes, including bichelate-α, bichelate-β and monochelate. Among these modes, the bichelate-α and monochelate modes were observed in **1** and **2**, respectively. Cyclic voltammetry revealed two irreversible reduction waves corresponding to L/L^{-1} (−1.75 V) and L^{-1}/L^{-2} (−2.03 V) in L which was shifted to lower voltage after coordination in **1** ($E(L/L^{-1})$ −1.82 V, $E(L^{-1}/L^{-2})$ −2.23 V), while in **2** ($E(L/L^{-1})$ −1.77 V, $E(L^{-1}/L^{-2})$ −2.01 V) no significant shifts were observed. These results revealed interaction of the carbonyl group with cadmium is stronger than with silver. Similar result was observed for ν (C=O) in IR spectra of **1** and **2**.

Supplementary material

CCDC 870 934 and 870 935 for $[CdL_3][CdI_4]$ **(1)** and $[Ag(L)NO_3]_n$ **(2)**, respectively, contain the supplementary crystallographic data supplementary crystallographic data for this

paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK; Fax: +44(0)1223–336,033; E-mail: deposit@ccdc.cam.ac.uk]. Structure factor table is available from the authors.

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