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catena-Poly[[(di-2-pyridylamine)-silver(I)]-μ-nicotinato] and *catena*-poly[[(di-2-pyridylamine)silver(I)]-μ-2,6-dihydroxybenzoato]

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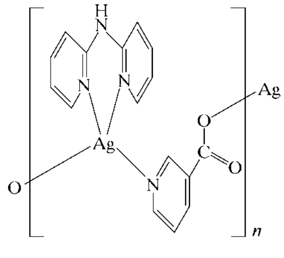
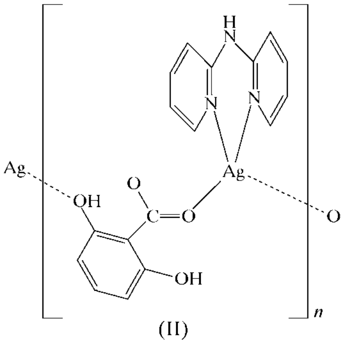
In *catena*-poly[[(di-2-pyridylamine-κ^2N,N')silver(I)]-μ-nicotinato-$\kappa^2N:O$], $[Ag(C_6H_4NO_2)(C_{10}H_9N_3)]_n$, the Ag^I atom is tetracoordinated by two N atoms from the di-2-pyridylamine (BPA) ligand [Ag—N = 2.3785 (18) and 2.3298 (18) Å] and by one N atom and one carboxylate O atom from nicotinate ligands [Ag—N = 2.2827 (15) Å and Ag—O = 2.3636 (14) Å]. Bridging by nicotinate N and O atoms generates a polymeric chain structure, which extends along [100]. The carboxyl O atom not bonded to the Ag atom takes part in an intrachain C—H$\cdots$O hydrogen bond, further stabilizing the chain. Pairs of chains are linked by N—H$\cdots$O hydrogen bonds to generate ribbons. There are no π–π interactions in this complex. In *catena*-poly[[(di-2-pyridylamine-κ^2N,N')silver(I)]-μ-2,6-dihydroxybenzoato-$\kappa^2O^1:O^2$], $[Ag(C_7H_5O_4)(C_{10}H_9N_3)]_n$, the Ag^I atom has a distorted tetrahedral coordination, with three strong bonds to two pyridine N atoms from the BPA ligand [Ag—N = 2.286 (5) and 2.320 (5) Å] and to one carboxylate O atom from the 2,6-dihydroxybenzoate ligand [Ag—O = 2.222 (4) Å]; the fourth, weaker, Ag-atom coordination is to one of the phenol O atoms [Ag$\cdots$O = 2.703 (4) Å] of an adjacent moiety, and this interaction generates a polymeric chain along [100]. Pairs of chains are linked about inversion centers by N—H$\cdots$O hydrogen bonds to form ribbons, within which there are π–π interactions. The ribbons are linked about inversion centers by pairs of C—H$\cdots$O hydrogen bonds and additional π–π interactions between inversion-related pairs of 2,6-dihydroxybenzoate ligands to generate a three-dimensional network.

Comment

Silver(I) complexes with Ag—N bonds have been found to show effective antimicrobial activity (Spadaro *et al.*, 1974; Nomiya *et al.*, 1997), and silver compounds with pyridine or its derivatives have attracted attention recently (Zhu *et al.*, 2001, 2003; Bi *et al.*, 2002; Kristiansson, 2000). Among the compounds containing a pyridine ring, nicotinic acid (3-pyridinecarboxylic acid, niacin or vitamin B; henceforth NA) plays important roles in metabolism. Dihydroxybenzoic acids are known to be strong antioxidants (Maoka *et al.*, 1997). As one example, 2,6-dihydroxybenzoic acid (2,6-DHB) is known to have a cytotoxic effect on tumor cells at low pH values when mixed with acetylsalicylic acid (Kreutz, 1998). Moreover 2,6-DHB always shows versatile coordination modes in its complexes. We report here the structures of two Ag^I complexes, *viz*. compound (I) with NA and the bidentate pyridine-based ligand 2,2′-bipyridylamine (BPA), *viz*. $[Ag(NA)(BPA)]_n$, and compound (II) with 2,6-DHB and BPA, *viz*. $[Ag(2,6\text{-DHB})(BPA)]_n$.



(I)



(II)

Compound (I) comprises a one-dimensional polymer chain (Fig. 1), with each Ag^I atom coordinated to two N atoms from a BPA ligand, one N atom from a nicotinate ligand and one carboxylate O atom from another nicotinate ligand [at $(1 + x, y, z)$], as shown in Fig. 1; geometric details are given in Table 1. The coordination geometry of the Ag^I ion is best described as distorted tetrahedral. The carboxyl atom that is not bonded to the Ag atom (O1) takes part in an intrachain C—H$\cdots$O hydrogen bond, further stabilizing the chain (Table 2).

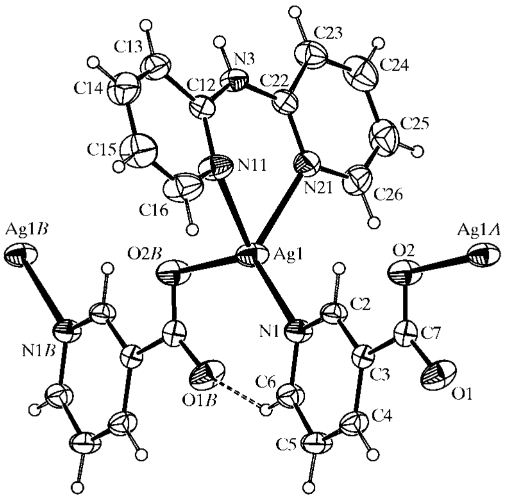


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of part of the polymeric chain in (I), with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. [Symmetry codes: (*A*) $x - 1, y, z$; (*B*) $1 + x, y, z$.]

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The coordination mode of (I) can be compared with some previous findings for silver(I)–nicotinic acid systems. In *catena*-(pyridine-3-carboxylato-*O*,*O*′)silver(I) (Smith & Reddy, 1994), the Ag^{I} ion has a trigonal coordination geometry, being connected to three nicotinate residues, two *via* carboxylate O atoms and the third through the pyridine N atom [Ag—O = 2.258 (8) and 2.280 (8) Å, and Ag—N = 2.362 (10) Å]; in ammonium bis(pyridine-3-carboxylato-*O*,*N*,*N*′)silver(I) monohydrate (Smith & Reddy, 1994), the Ag^{I} ion again has three-coordinate distorted trigonal–planar geometry and is bonded to two pyridine N atoms and one carboxylate O atom from three independent nicotinate ligands [Ag—N = 2.248 (3) and 2.269 (3) Å, and Ag—O = 2.342 (2) Å]. The Ag^{I} coordination mode in (I) is also different from that reported in *catena*-bis(pyridine-3-carboxylato-*N*,*N*′)silver(I) (Käll *et al.*, 2001), where the Ag^{I} ion has distorted octahedral coordination geometry, lies on an inversion center with the N atoms in axial positions (Ag—N = 2.234 Å and N—Ag—N = 180°) and is bonded weakly to four carboxylate O atoms from four independent nicotinate molecules (Ag—O = 2.803 and 2.821 Å). The Ag—N distances in (I) are slightly longer than those in silver complexes of other pyridine derivatives, such as bis(3-amino-2-chloropyridine-κN)silver(I) perchlorate [2.197 (4)–2.199 (4) Å; Li *et al.*, 2002], bis(2-aminopyridine-κN^{1})(benzoato-κO)silver(I) [2.205 (4)–2.230 (3) Å; Zhu *et al.*, 2003] and *catena*-poly[[silver(I)-μ-4,4′-bipyridine] nitrate] [2.211 (4) Å; Bi *et al.*, 2002].

In the nicotinate ligand, the plane of the carboxyl group (C3/C7/O1/O2) is rotated 10.7 (1)° around the exocyclic C3—C7 bond out of the N1/C2–C7 plane. The two pyridine rings in the BPA ligand form an interplanar angle of 9.7 (1)°, and the six-membered Ag1/N11/C12/N3/C22/N21 ring has a slightly deformed envelope conformation, with atom Ag1 as the flap.

In the crystal structure (Fig. 2), pairs of inversion-related chains are linked by N—H···O hydrogen bonds (Table 2) to generate ribbons extending along [100]. Calculations with *PLATON* (Spek, 2003) show that there are only van der Waals interactions between the ribbons.

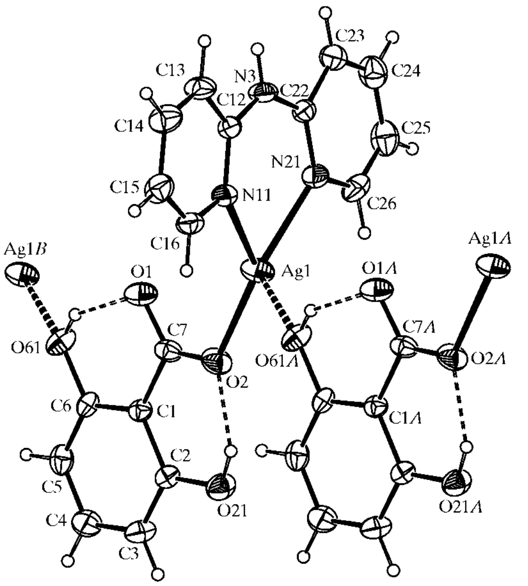

Figure 3
An *ORTEP*-3 (Farrugia, 1997) drawing of part of the polymeric chain in (II), with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. [Symmetry codes: (*A*) *x* − 1, *y*, *z*; (*B*) 1 + *x*, *y*, *z*.]

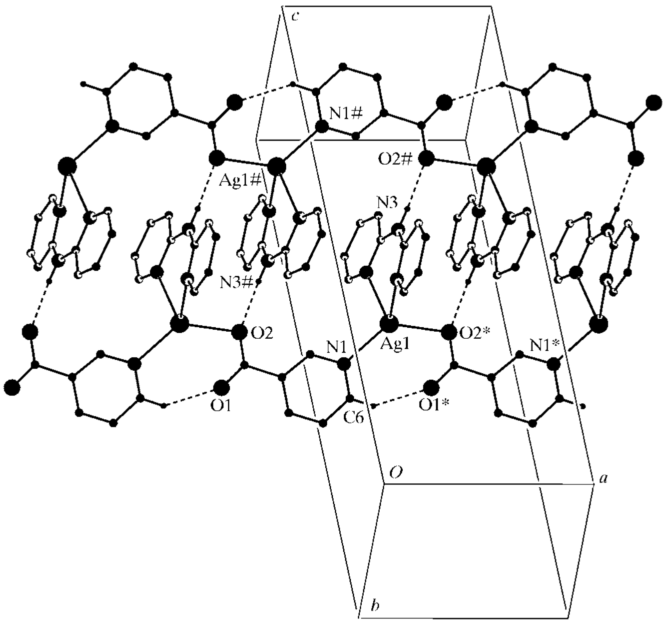

Figure 2
A view of a pair of inversion-related chains linked by N—H···O hydrogen bonds to generate a ribbon extending in the *a* direction. Hydrogen bonds are indicated by broken lines. [Symmetry codes: (#) −*x*, −*y*, 1 − *z*; (*) 1 + *x*, *y*, *z*.]

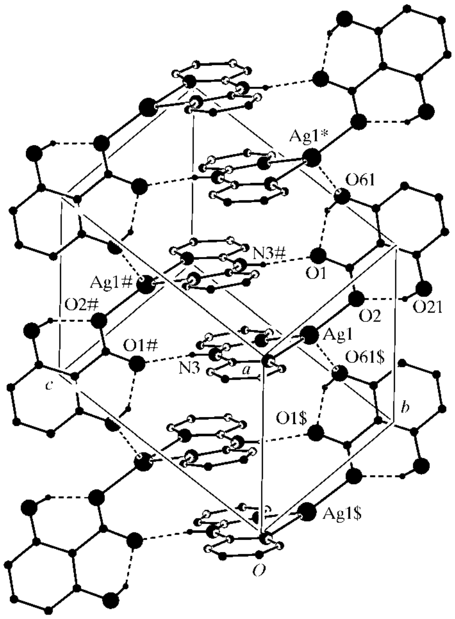

Figure 4
A view of a pair of inversion-related chains linked by N—H···O hydrogen bonds to generate a ribbon extending in the *a* direction. The weak Ag···O contact and hydrogen bonds are indicated by broken lines. [Symmetry codes: (#) 1 − *x*, 1 − *y*, 1 − *z*; (*) 1 + *x*, *y*, *z*; ($) *x* − 1, *y*, *z*.]

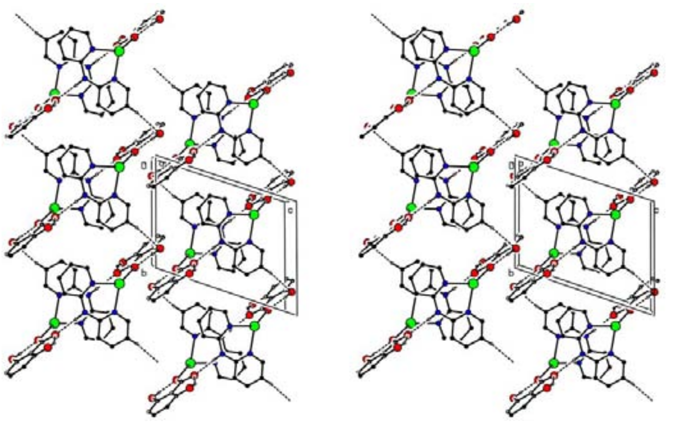

Figure 5
A stereoview along the *a* direction of part of the structure of (II), showing π–π interactions between inversion-related pairs of BPA ligands and between inversion-related pairs of 2,6-DHB ligands.

In complex (II) (Fig. 3), the Ag^{I} atom has a distorted tetrahedral coordination, with three strong bonds to two pyridine N atoms from the BPA ligand and one carboxylate O atom from the 2,6-DHB ligand; the fourth, weaker, Ag-atom coordination is to one of the phenol O atoms (O61) of an adjacent moiety (Table 3), thus generating a polymeric chain along [100]. BPA atoms N11 and N12 together with carboxyl atom O2 are the atoms that are strongly bonded to atom Ag1; these atoms define a trigonal plane, with atom Ag1 lying 0.319 (2) Å from the plane.

In the 2,6-DHB ligand, the plane of the carboxyl group (C3/C7/O1/O2) is rotated 2.4 (3)° around the exocyclic C1—C7 bond out of the C1–C7 plane. Both phenol OH groups form intramolecular O—H···O hydrogen bonds (Table 4) with adjacent carboxyl O atoms. The two pyridine rings in the BPA ligand form an interplanar angle of 5.2 (2)°, and as in (I), the six-membered Ag1/N11/C12/N3/C22/N21 ring has a slightly deformed envelope conformation, with atom Ag1 as the flap. The participation of the BPA ligand means that the Ag coordination environment in (II) is (as expected) completely different from the dimer-bridged coordination mode reported for the 2,6-DHB ligand in bis(μ_2-2,6-dihydroxybenzoato-*O*,*O*′)disilver(I) (Smith *et al.*, 1988).

In the crystal structure of (II), inversion-related chains are linked [as in (I)] by N—H···O hydrogen bonds involving the BPA N3—H3 group and carboxyl atom O1 of an adjacent moiety (Table 1), thus generating ribbons extending along [100], as shown in Fig. 4. Also present in these ribbons are π–π interactions between inversion-related BPA ligands. The distance between the ring centroids of the N11/C12–C16 and N21/C22–C26 [at $(1 - x, 1 - y, 1 - z)$] BPA pyridine rings is 3.616 Å and the shortest atom–atom separation is 3.466 (9) Å, between atoms C12 and C22$(1 - x, 1 - y, 1 - z)$. This ring overlap can be seen clearly in Fig. 5, which also shows that the ribbons are linked by an inter-ribbon C—H···O hydrogen bond involving the C25—H25 group and phenol atom O21$(x, y - 1, z)$, which is not involved in any Ag contact (see Table 4). There are, in addition, a second set of π–π interactions between inversion-related 2,6-DHB ligands. The centroid of the C1–C6 aromatic ring at (x, y, z) is 3.763 Å from the centroid of the same ring at $(2 - x, 2 - y, -z)$; the distance between these parallel rings is 3.425 Å and the shortest C···C contact is 3.413 (3) Å, between atoms C2 and C6$(2 - x, 2 - y, -z)$. The overall effect of all these interactions is to generate a three-dimensional network.

Experimental

Thin colorless needle-shaped crystals of (I) were obtained by slow evaporation of an aqueous solution (containing a small amount of methanol) of a mixture of nicotinic acid, 2,2′-bipyridineamine and $AgNO_3$ (molar ratio 1:1:1) at room temperature. Colorless prismatic crystals of (II) were obtained by slow evaporation of a mixture of 2,6-dihydroxybenzoic acid, 2,2′-bipyridineamine and $AgNO_3$ (molar ratio 4:4:1) in methanol/water (80%) at room temperature.

Compound (I)

Crystal data

$[Ag(C_6H_4NO_2)(C_{10}H_9N_3)]$
$M_r = 401.17$
Monoclinic, $P2_1/n$
$a = 7.9623$ (1) Å
$b = 8.9487$ (1) Å
$c = 21.887$ (1) Å
$\beta = 96.000$ (1)°
$V = 1550.95$ (8) Å^3
$Z = 4$
$D_x = 1.718$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 577 reflections
$\theta = 3.0$–27.5°
$\mu = 1.31$ mm^{-1}
$T = 296$ K
Needle, colorless
0.30 × 0.10 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.649$, $T_{max} = 0.877$
15 058 measured reflections
3530 independent reflections
2779 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 27.6°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.055$
$S = 0.90$
3530 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Ag1—N1	2.2827 (15)	Ag1—N21	2.3298 (18)
Ag1—N11	2.3785 (18)	Ag1—O2^{i}	2.3636 (14)
N1—Ag1—N21	125.12 (6)	N1—Ag1—N11	105.36 (6)
N1—Ag1—O2^{i}	128.08 (5)	N21—Ag1—N11	77.97 (6)
N21—Ag1—O2^{i}	99.28 (6)	O2^{i}—Ag1—N11	109.43 (6)

Symmetry code: (i) $1 + x, y, z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O2^{ii}	0.86	2.03	2.894 (2)	177
C6—H6···O1^{i}	0.93	2.29	3.096 (2)	144

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, -y, 1 - z$.

Compound (II)

Crystal data

$[Ag(C_7H_5O_4)(C_{10}H_9N_3)]$
$M_r = 432.18$
Triclinic, $P\overline{1}$
$a = 7.56$ (1) Å
$b = 9.23$ (1) Å
$c = 12.01$ (2) Å
$\alpha = 71.29$ (5)°
$\beta = 82.87$ (5)°
$\gamma = 87.44$ (5)°
$V = 787.6$ (19) Å^3
$Z = 2$
$D_x = 1.822$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6495 reflections
$\theta = 3.1$–27.6°
$\mu = 1.31$ mm^{-1}
$T = 296$ K
Prism, colorless
0.30 × 0.15 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.672$, $T_{max} = 0.878$
7753 measured reflections
3567 independent reflections
2402 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.153$
$S = 1.02$
3567 reflections
228 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -1.28$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Ag1—N11	2.320 (5)	Ag1—O2	2.222 (4)
Ag1—N21	2.286 (5)	Ag1—O61^{iii}	2.703 (4)
O2—Ag1—N21	133.99 (15)	O2—Ag1—O61^{iii}	95.21 (16)
O2—Ag1—N11	138.13 (16)	N21—Ag1—O61^{iii}	120.49 (15)
N11—Ag1—N21	80.97 (15)	N11—Ag1—O61^{iii}	78.52 (14)

Symmetry code: (iii) $x - 1, y, z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O21—H21···O2	0.82	1.81	2.538 (6)	146
O61—H61···O1	0.82	1.80	2.525 (6)	147
N3—H3···O1^{iv}	0.86	2.08	2.927 (6)	170
C25—H25···O21^{v}	0.93	2.60	3.519 (8)	171

Symmetry codes: (iv) $1 - x, 1 - y, 1 - z$; (v) $x, y - 1, z$.

For both (I) and (II), all H atoms were clearly visible in difference Fourier maps. H atoms were then allowed for as riding atoms in the refinements, with C—H distances of 0.93 Å, N—H distances of 0.86 Å and O—H distances of 0.82 Å, and with U_{iso}(H) values of $1.2U_{eq}$(C,N) and $1.5U_{eq}$(O).

For compound (I), data collection: *RAPID-AUTO* (Rigaku, 2003); cell refinement: *RAPID-AUTO*. For compound (II), data collection: *CrystalStructure* (Rigaku/MSC, 2004) and *CRYSTALS* (Watkin *et al.*, 1996); cell refinement: *CrystalStructure* and *CRYSTALS*. For both compounds, data reduction: *CrystalStructure* and *CRYSTALS*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999) and *DIRDIF*99 (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) and *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *WordPerfect*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1780). Services for accessing these data are described at the back of the journal.

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