

A stair-like two-dimensional silver(I) coordination polymer of *N'*-(3-cyanobenzylidene)nicotinothiazide

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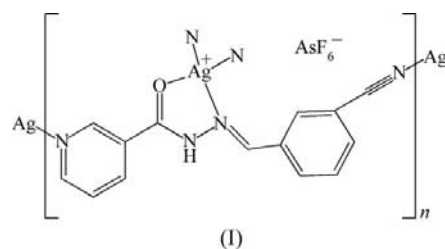
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The structure of the title compound, poly[[[μ_3 -*N'*-(3-cyanobenzylidene)nicotinothiazide]silver(I)] hexafluoroarsenate], {[Ag(C₁₄H₁₀N₄O)](AsF₆)_n}, at 173 K exhibits a novel stair-like two-dimensional layer and a three-dimensional supramolecular framework through C—H···Ag hydrogen bonds. The Ag^I cation is coordinated by three N atoms and one O atom from *N'*-(3-cyanobenzylidene)nicotinothiazide (*L*) ligands, resulting in a distorted tetrahedral coordination geometry. The organic ligand acts as a μ_3 -bridging ligand through the pyridyl and carbonitrile N atoms and deviates from planarity in order to adapt to the coordination geometry. Two ligands bridge two Ag^I cations to construct a small 2+2 Ag₂L₂ ring. Four ligands bridge one Ag^I cation from each of four of these small rings to form a large grid. An interesting stair-like two-dimensional (3,6)-net is formed through Ag^I metal centres acting as three-connection nodes and through *L* molecules as tri-linkage spacers.

Comment

The design and construction of novel coordination polymers are very important parts of crystal engineering, not only for functional materials purposes but also because of the favourable architectures and topologies of these polymers (Murray *et al.*, 2009; Eddaoudi *et al.*, 2001). Metal centres as connecting nodes and organic bridging ligands as spacers should be cogitatively selected before studies. For metal centres, silver ions are widely used because silver coordinating polymers possess strong luminescent emissions and antibiotic properties. In addition, the coordination number and metal stereochemistry for silver(I) is quite variable (Catalano *et al.*, 1999; Dong *et al.*, 2004; Zheng *et al.*, 2003; Schottel *et al.*, 2005). Furthermore, there are many significant inter- and intramolecular interactions between silver centres (Ag···Ag metal interactions), and between silver and other elements, such as

organic aromatic π systems (Ag··· π interactions; Jung *et al.*, 2004), O atoms (Ag···O interactions; Wang & Mak, 2002), S atoms (Ag···S interactions; Wang *et al.*, 2006), halogen (*X*) atoms [*X* = F, Cl, Br and I; Ag···*X* interactions; Blake *et al.*, 2000], and rare H, C, CH₂ and CH₃ (C—H···Ag weak hydrogen bonds, Ag···H—C agostic interactions and Ag···C organometallic interactions; Clarke *et al.*, 2004; McMorran & Steel, 2002; Liu *et al.*, 2006; Zhao & Mak, 2007). For organic ligands, pyridyl–carbonitrile ligands with labile coordinating properties and different coordinating groups with different coordinating abilities towards Ag atoms were used in some of our studies (Niu *et al.*, 2007, 2008). For the series of Schiff base ligands synthesized from cyanobenzaldehyde and pyridylhydrazone, we noticed that if we changed the position of the N atom on the pyridyl ring, the molecular or supramolecular structures of the silver coordination compounds were different. Thus, it should be reasonable to assume that, if the position of the carbonitrile group on the benzene ring is changed, a new silver coordinating compound with an unexpected structure might be obtained.



We report here the structure of a novel silver coordination polymer of the new bridging ligand *N'*-(3-cyanobenzylidene)nicotinothiazide (*L*), namely {[Ag(*L*)](AsF₆)_n}, (I). Its crystal structure determined by X-ray diffraction shows it to possess a novel stair-like two-dimensional layer structure. More interestingly, weak C—H···Ag hydrogen bonds were found connecting these two-dimensional layers, forming a three-dimensional framework.

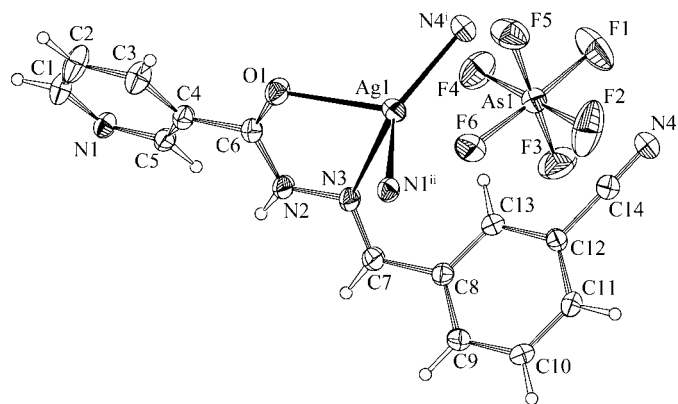


Figure 1
The local coordination around the Ag^I centre in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. For symmetry codes, see Table 1.

metal-organic compounds

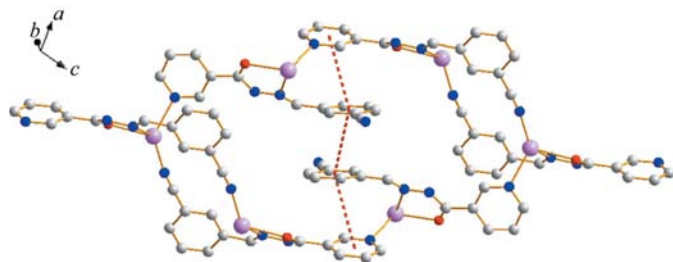


Figure 2
A ball-and-stick diagram showing the large ring and the intermolecular π - π interactions (dashed lines).

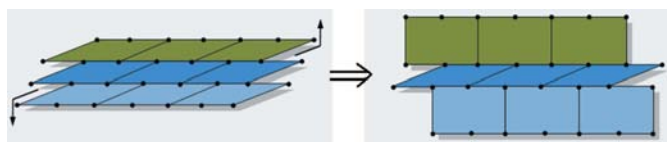


Figure 3
The transition from the usual brick-wall (3,6)-net (left) to a stair-like framework (right).

In (I), the silver ion is four-coordinated by one O atom and one N atom (O1 and N3) from the hydrazide segment of the ligand and by the pyridyl and carbonitrile N atoms (N1ⁱⁱ and N4ⁱ; for symmetry codes, see Table 1) from two other bridging ligands, giving a distorted tetrahedral coordination geometry (Fig. 1). Ligand donor atoms O1 and N3 are coordinated to the silver ion in a bidentate coordinating mode to form a planar five-membered chelate ring (Ag1/O1/C6/N2/N3). The Ag–O bond distance is 2.415 (2) Å, and the Ag–N bond distances range from 2.151 (3) to 2.462 (2) Å (Table 1). The Ag–N(carbonitrile) bond distance is the shortest. The distortion of the tetrahedral coordination geometry is largely a result of the small bite angle of the bidentate coordination [angles about the metal centre = 67.08 (7)–133.08 (10)°; Table 1]. The

hydrazide ligand molecule is distorted from planarity in accommodating the metal coordination centres. The Ag1/O1/C6/N2/N3 ring is not coplanar with the benzene ring of the same ligand [the dihedral angle is 47.15 (2)°; Fig. 2]. The plane of the pyridyl ring is also twisted slightly from that of the above-mentioned chelate ring and makes a dihedral angle of 74.91 (2)° with the plane of the aromatic ring. Two *L* molecules bridge pairs of Ag coordination centres through the carbonitrile N atom and the primary bidentate chelate ligand interaction, to form a small centrosymmetric 2+2 Ag₂L₂ ring. The Ag...Ag separation in one ring is 6.5147 (6) Å. Four of these small rings are linked to each other by pyridyl atom N1, coordinating to Ag atoms in adjacent rings to produce a large nearly rectangular grid. Thus, two Ag atoms from different 2+2 rings are bridged by the entire length of *L* via the pyridyl and carbonitrile N atoms, and this bridging ligand is not planar. The Ag...Ag separation for atoms bridged in this way is 13.2985 (9) Å. The distance between two neighbouring Ag atoms bridged via the bidentate hydrazide O1 and N3 atoms and the monodentate pyridyl N1 atom is 8.5129 (5) Å. The spaces within this grid are not void but occupied by two parallel benzene rings, which are also parallel to two pyridyl rings of the large grid. Weak π - π interactions exist between two neighbouring parallel benzene rings, and between neighbouring parallel benzene and pyridyl rings, with centroid-centroid distances of about 3.9 Å, and interplanar angles of 0° and about 14°, respectively. These weak interactions help the stability of the large grid constructed by the deformed *L* molecules. The AsF₆[−] counter-anions are located on the outside of the grids and are associated with the hydrazide chains through N–H...F hydrogen bonds (Table 2).

It is noteworthy that a stair-like two-dimensional (3,6)-net is formed through Ag metal centres acting as three-connection nodes and *L* molecules as tri-linkage spacers using two bottom (N1 and N4) and one middle (N3 or O1) coordinating atoms. These nets are unlike most reported two-dimensional planar

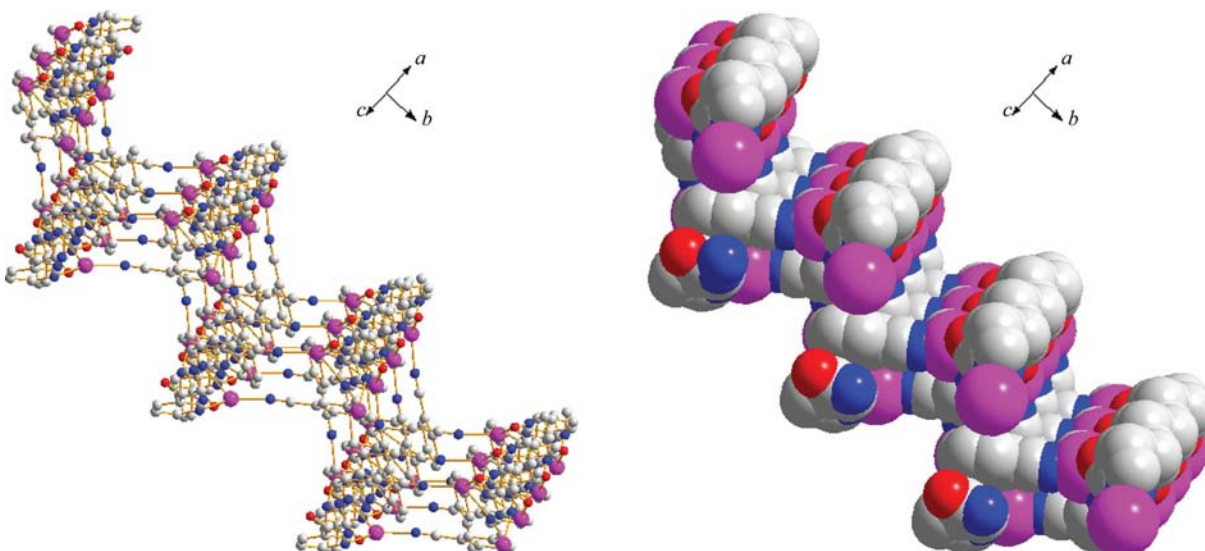


Figure 4
Ball-and-stick (left) and space-filling (right) diagrams, showing the stair-like framework of (I).

brick-wall (3,6)-nets but can be seen as deformed or even folded planar (3,6)-nets, driven by the tetrahedral coordination environment of the metal centres, instead of the square-planar type, together with the deformation from planarity of the *L* ligand. Two adjacent ladders bend in two different directions, one up and the other down, both by nearly 90° (Fig. 3). Deformed hydrazide chains and pyridyl rings coordinating to Ag atoms are located at the corners of the steps, whereas carbonitrile chains link two edges, constructing the horizontal and vertical parts of the steps (Fig. 4).

Another striking feature of the structure of this compound is the occurrence of the rare intermolecular C—H...Ag interactions between two neighbouring stair-like layers. The intermolecular distances indicate the presence of obvious close complementary C—H...M close interactions between the metal centres and the pyridyl ring H atoms [Ag...H = 2.85 Å, Ag...C = 3.576 (4) Å and C—H...Ag = 135°]. From the above-mentioned bond distances and angle, such C—H...Ag close interactions should be described as weak intermolecular C—H...M hydrogen bonding, as described previously (Thakur & Desiraju, 2005). Furthermore, donors and acceptors involve two separate coordination centres, strengthening contacts between the two components (Fig. 5). Although neighbouring stair-like layers connected via C—H...Ag interactions produce grid-like one-dimensional tunnels with diameters from about 0.6–1.0 nm, AsF₆[−] counteranions occupy these tunnels, reducing the gas absorption ability of the solid material. However, ion exchange from AsF₆[−] anions to other analogues, such as PF₆[−], is possible.

Finally, inter- or intramolecular C—H...Ag interactions were found in only a few silver compounds and act as connectors to link some finite components (e.g. {[AgL²](ClO₄)₂}, L² = 9-[3-(2-pyridyl)pyrazol-1-yl]acridine; Ag...H = 2.657–2.706 Å, Ag...C = 3.198–3.231 Å and C—H...Ag = 116.60–117.73°; Clarke *et al.*, 2004; McMorran & Steel, 2002; Liu *et al.*, 2006; Zhao & Mak, 2007). However, to the best of our knowledge, no previous studies have found C—H...Ag interactions that connect infinite one-dimensional chains or two-dimensional layers of silver coordination polymers to construct higher-dimensional frameworks. The present work may therefore provide a new method for the construction of supramolecular high-dimensional frameworks.

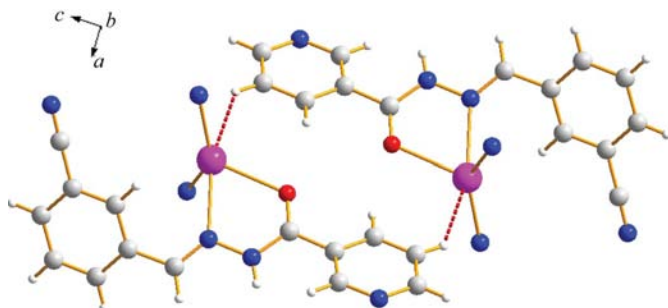


Figure 5
A ball-and-stick diagram showing the rare intermolecular C—H...Ag hydrogen bonds (dashed lines) in (I).

Experimental

A solution of AgAsF₆ (0.1 mmol) in methanol (10 ml) was carefully layered on a solution of *N'*-(3-cyanobenzylidene)nicotinothiazide (0.1 mmol) in chloroform (10 ml) in a straight glass tube. After about two weeks, single crystals suitable for X-ray analysis appeared at the boundary between the two layers (yield *ca* 40%). Analysis calculated for C₁₄H₁₀AgAsF₆N₄O: C 30.74, H 1.84, N 10.24%; found: C 30.89, H 1.77, N 10.27%. IR (KBr, ν , cm^{−1}): 3339 (*m*), 3068 (*w*), 2267 (*m*), 1663 (*s*), 1598 (*w*), 1534 (*m*), 1476 (*w*), 1429 (*w*), 1362 (*w*), 1290 (*m*), 1164 (*w*), 1145 (*w*), 955 (*w*), 810 (*w*), 705 (*vs*), 583 (*w*), 530 (*w*).

Crystal data

[Ag(C ₁₄ H ₁₀ N ₄ O)](AsF ₆)	<i>V</i> = 1743.3 (2) Å ³
<i>M_r</i> = 547.05	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 12.7022 (10) Å	μ = 3.11 mm ^{−1}
<i>b</i> = 10.6710 (8) Å	<i>T</i> = 173 K
<i>c</i> = 13.5477 (11) Å	0.29 × 0.22 × 0.20 mm
β = 108.316 (1)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	11028 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2005)	3988 independent reflections
<i>T</i> _{min} = 0.466, <i>T</i> _{max} = 0.575	3330 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.021

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.030	244 parameters
<i>wR</i> (<i>F</i> ²) = 0.083	$\Delta\rho_{\max}$ = 0.48 e Å ^{−3}
<i>S</i> = 1.03	$\Delta\rho_{\min}$ = −0.64 e Å ^{−3}
3988 reflections	

Table 1

Selected geometric parameters (Å, °).

Ag1—N4 ⁱ	2.151 (3)	Ag1—O1	2.415 (2)
Ag1—N1 ⁱⁱ	2.293 (2)	Ag1—N3	2.462 (2)
N4 ⁱ —Ag1—N1 ⁱⁱ	133.08 (10)	N4 ⁱ —Ag1—N3	129.89 (10)
N4 ⁱ —Ag1—O1	116.06 (10)	N1 ⁱⁱ —Ag1—N3	86.31 (9)
N1 ⁱⁱ —Ag1—O1	104.56 (9)	O1—Ag1—N3	67.08 (7)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H14...F5 ⁱⁱⁱ	0.88	2.25	2.975 (4)	140
N2—H14...F1 ⁱⁱⁱ	0.88	2.47	3.308 (4)	159

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

H atoms were placed in calculated positions and refined using a riding model [C—H = 0.95 Å, N—H = 0.88 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C,N)]. The highest peak in the final difference Fourier map was 1.02 Å from atom F1 and the deepest hole was 0.66 Å from Ag1, and the map was otherwise featureless.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 2005); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3016). Services for accessing these data are described at the back of the journal.

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