

catena-Poly[[[(iminodiacetato- κ O)-silver(I)]- μ_3 -2-aminopyrimidine- κ^3 N¹:N²:N³] monohydrate]: a one-dimensional silver(I) coordination polymer with mixed ligandsDi Sun,^a Geng-Geng Luo,^a Rong-Bin Huang,^{a*} Na Zhang^a and Lan-Sun Zheng^b^aDepartment of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China, and ^bState Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, People's Republic of China

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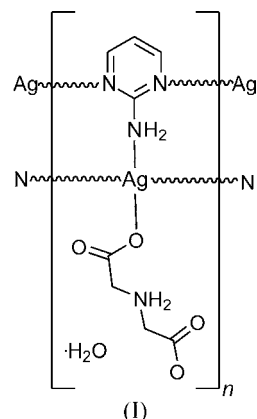
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The title compound, $\{[\text{Ag}(\text{C}_4\text{H}_6\text{NO}_4)(\text{C}_4\text{H}_5\text{N}_3)] \cdot \text{H}_2\text{O}\}_n$, was synthesized by the reaction of silver(I) nitrate with 2-aminopyrimidine and iminodiacetic acid. X-ray analysis reveals that the crystal structure contains a one-dimensional ladder-like Ag^{I} coordination polymer and that $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonding results in a three-dimensional network. The Ag^{I} centre is four-coordinated by three N atoms from three different 2-aminopyrimidine ligands and one O atom from one iminodiacetate ligand. Comparison of the structural features with previous findings suggests that the existence of a second ligand plays an important role in the construction of such polymer frameworks.

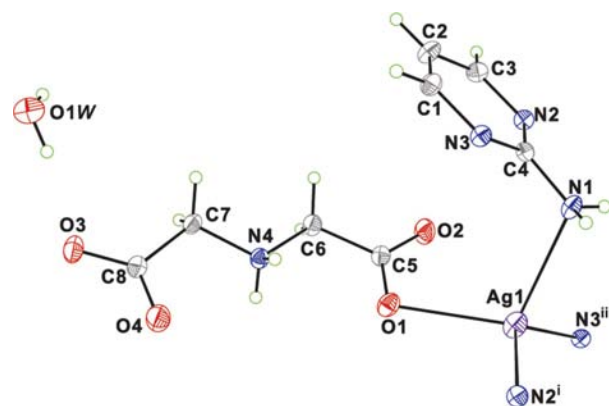
Comment

Pyrimidine and aminopyrimidine derivatives are biologically important compounds as they occur in nature as components of nucleic acids. Some aminopyrimidine derivatives are used as antifolate drugs (Hunt *et al.*, 1980; Baker & Santi, 1965). They are also used in the development of polymeric metal-organic frameworks (MOFs), owing to their demonstrated ability to form very stable hydrogen-bonded chain arrays *via* their stereochemically associative amino groups and heterocyclic N atoms, and to coordinate to metal centres through various bonding modes (Aoki *et al.*, 1994; Blake *et al.*, 1999). As a soft acid, the Ag^{I} ion is a favourable and fashionable building block or connecting node for coordination polymers, not only due to its ready coordination by soft bases such as unsaturated N atoms (Carlucci *et al.*, 1995), but also because closed-shell d^{10} $\text{Ag} \cdots \text{Ag}$ interactions can often give rise to intriguing supramolecular motifs (Blake *et al.*, 2000; Melcer *et al.*, 2001). Recently, we have undertaken a series of investi-

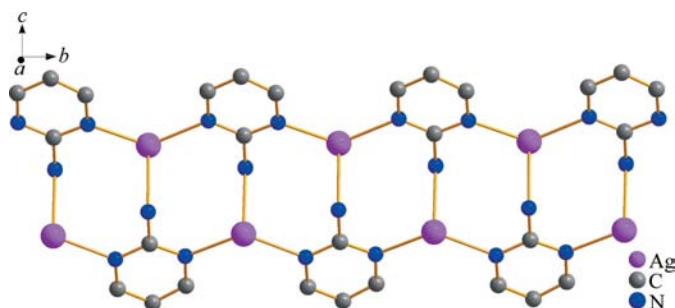
gations into the assembly of Ag^{I} ions with different aminopyrimidine derivatives (Luo, Huang, Chen *et al.*, 2008; Luo, Huang, Zhang *et al.*, 2008; Luo *et al.*, 2009), with the principal aim of obtaining supramolecular compounds or ordered coordination polymers, and found that in the resulting structures, aminopyrimidine derivatives often adopt mono- and bidentate coordination modes with Ag^{I} ions *via* their pyrimidine N atoms. However, tridentate coordination by pyrimidine and amino N atoms is still quite rare (Wang *et al.*, 2006). The introduction of a second ligand such as a dicarboxylic acid dramatically alters the structures and properties of these complexes. Inspired by these results, we employed 2-aminopyrimidine as a tridentate ligand and incorporated iminodiacetic acid into the previously known Ag^{I} -2-aminopyrimidine system, and successfully obtained the title compound, (I), a novel one-dimensional ladder coordination polymer.



Single-crystal X-ray diffraction study reveals that compound (I) comprises one Ag^{I} centre, one 2-aminopyrimidine ligand, one iminodiacetate anion and one uncoordinated water molecule. As shown in Fig. 1, the four-coordinated Ag^{I} atom adopts a strongly distorted tetrahedral geometry (Table 1) and is coordinated by two pyrimidine N

**Figure 1**

The structure of (I), showing the atom-numbering scheme and the coordination environment at the Ag^{I} centre. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $1 - x, y - \frac{1}{2}, -z + \frac{1}{2}$.]

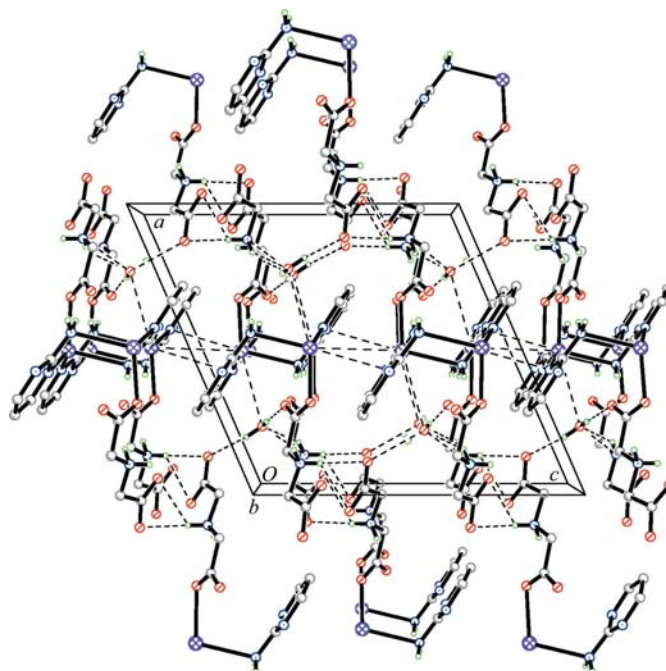
**Figure 2**

A perspective view of the one-dimensional ladder of (I), which runs parallel to the *b* axis. H atoms have been omitted for clarity.

atoms from two independent 2-aminopyrimidine ligands, one amino N atom from another 2-aminopyrimidine ligand and one O atom from an iminodiacetate anion. The widest $\text{N3}^i\text{—Ag1—O1}$ angle is $133.95(6)^\circ$ and the remaining angles are in the range $89.22(6)$ – $126.98(7)^\circ$. It is noteworthy that the $\text{Ag—N}_{\text{amino}}$ distance [$\text{Ag1—N1} = 2.604(2) \text{ \AA}$] is significantly longer than the $\text{Ag}\cdots\text{N}_{\text{pyrimidine}}$ distances [$\text{Ag1—N3}^{ii} = 2.2872(19) \text{ \AA}$ and $\text{Ag1—N2}^i = 2.3312(19) \text{ \AA}$; symmetry codes: (i) $1 - x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $1 - x, y - \frac{1}{2}, -z + \frac{1}{2}$]. This difference may be partly due to electronic effects between the amino N and pyrimidine N atoms. A pair of lone electrons on the amino N atom is partially delocalized into the pyrimidine ring, which makes the amino N atom less basic than the pyrimidine N atoms. Interestingly, aminopyrimidine derivatives often adopt *N*-monodentate and *N,N'*-bidentate coordination modes with Ag^{I} via their pyrimidine N atoms, and the only example adopting tridentate coordination was reported by Wang *et al.* (2006).

As shown in Fig. 2, the 2-aminopyrimidine ligands of (I) are coordinated to the Ag^{I} centres in this *N:N':N''*-coordination mode to form a one-dimensional ladder structure, in which the iminodiacetate anion adopts a bis-monodentate coordination mode to Ag^{I} , precluding the extension of the motif into two dimensions. It is noteworthy that the N atoms of the iminodiacetate anions are protonated and so do not participate in coordination to any metal centre. All the carboxylate groups are deprotonated, fulfilling the requirement for overall charge neutrality.

In each one-dimensional ladder, Ag^{I} ions and 2-aminopyrimidine ligands are interlinked to form chair-like eight-membered M_2L_2 binuclear rings. Two kinds of intermolecular hydrogen bonds are observed in neighbouring ladders. $\text{N—H}\cdots\text{O}$ hydrogen bonds have $\text{N}\cdots\text{O}$ distances in the range $2.781(3)$ – $3.070(3) \text{ \AA}$. The N atoms of the amino group of the 2-aminopyrimidine ligands and protonated imino groups serve as donors, while the O atoms of the iminodiacetate anion and uncoordinated water molecule act as acceptors. $\text{O1W—H}\cdots\text{O}$ hydrogen bonds involve the O atoms of the iminodiacetate anion and the uncoordinated water molecule acting as acceptors and donors, respectively. These hydrogen bonds link the ladders into a three-dimensional framework, as shown in Fig. 3.

**Figure 3**

A schematic representation of the three-dimensional structure formed via hydrogen bonds (dashed lines), viewed down the *b* axis.

In conclusion, a new one-dimensional Ag^{I} coordination polymer with mixed *N*-donor and *O*-donor ligands shows rare *N:N':N''*-tridentate and *O*-monodentate coordination modes, respectively.

Experimental

All reagents and solvents were obtained commercially and used without further purification. Silver nitrate (170 mg, 1 mmol) and 2-aminopyrimidine (95 mg, 1 mmol) were dissolved in water (5 ml). To this solution was added a methanolic solution (5 ml) of iminodiacetic acid (133 mg, 1 mmol) with stirring. The mixture was stirred for about 20 min at room temperature to give a clear colourless solution. The resulting solution was kept in darkness for 4 d, after which time well-formed colourless block-shaped crystals of (I) were obtained. The product is insoluble in water and methanol.

Crystal data

$[\text{Ag}(\text{C}_4\text{H}_6\text{NO}_4)(\text{C}_4\text{H}_5\text{N}_3)]\cdot\text{H}_2\text{O}$
 $M_r = 353.09$
 Monoclinic, $P2_1/c$
 $a = 13.495(3) \text{ \AA}$
 $b = 6.5202(13) \text{ \AA}$
 $c = 14.103(3) \text{ \AA}$
 $\beta = 113.49(3)^\circ$

$V = 1138.1(4) \text{ \AA}^3$
 $Z = 4$
 Mo K_α radiation
 $\mu = 1.79 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 $0.50 \times 0.30 \times 0.30 \text{ mm}$

Data collection

Oxford Diffraction Gemini S Ultra diffractometer
 Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
 $T_{\text{min}} = 0.468$, $T_{\text{max}} = 0.615$
 (expected range = 0.444 – 0.584)

9403 measured reflections
 2230 independent reflections
 2013 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Table 1

Selected geometric parameters (Å, °).

Ag1—O1	2.4868 (19)	Ag1—N2 ⁱ	2.3312 (19)
Ag1—N1	2.604 (2)	Ag1—N3 ⁱⁱ	2.2872 (19)
O1—Ag1—N1	103.35 (7)	N1—Ag1—N2 ⁱ	99.65 (6)
O1—Ag1—N2 ⁱ	89.22 (6)	N1—Ag1—N3 ⁱⁱ	97.77 (6)
O1—Ag1—N3 ⁱⁱ	133.95 (6)	N2 ⁱ —Ag1—N3 ⁱⁱ	126.98 (7)

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.**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>
N1—H1A...O2 ⁱ	0.90	2.09	2.904 (3)	151
N1—H1B...O1 ⁱⁱ	0.90	2.00	2.896 (3)	178
N4—H4A...O1W ⁱⁱⁱ	0.90	2.03	2.781 (3)	140
N4—H4B...O4 ^{iv}	0.90	2.52	3.070 (3)	120
O1W—H1WA...O2 ^v	0.844 (10)	1.883 (13)	2.714 (3)	168 (4)
O1W—H1WB...O3	0.849 (10)	1.908 (12)	2.753 (3)	174 (5)

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x, -y + 1, -z$; (iv) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x, -y, -z$.**Refinement** $R[F^2 > 2\sigma(F^2)] = 0.025$ $wR(F^2) = 0.064$ $S = 1.08$

2230 reflections

171 parameters

2 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 0.84 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$

The aromatic and amino H atoms were generated geometrically (C—H = 0.93 Å and N—H = 0.90 Å) and allowed to ride on their parent atoms in riding-model approximations, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. After their location in difference maps, the positions and U_{iso} values of the water H atoms were refined, with the O—H distances restrained to 0.85 (1) Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduc-

tion: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3083). Services for accessing these data are described at the back of the journal.

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