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# *catena*-Poly[silver(I)-$\mu_2$-4,4′-bipyridine-$\kappa^2N$:$N'$-$\mu_3$-chlorido]: self-assembly of a two-dimensional bilayer silver(I) coordination polymer from AgCl and a bipodal spacer

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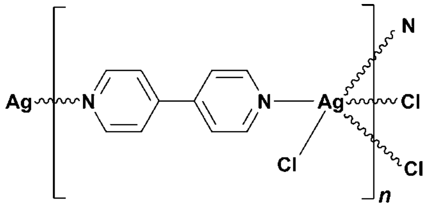
The title compound, $[\mathrm{AgCl}(\mathrm{C}_{10}\mathrm{H}_8\mathrm{N}_2)]_n$, was synthesized by reaction of silver(I) chloride with 4,4′-bipyridine (bipy) under ammoniacal conditions. The crystal structure reveals that the Ag and Cl atoms lie on twofold axes, while the bipy ligands also sit across twofold axes. The $\mathrm{Ag}^{\mathrm{I}}$ center is five-coordinated by three Cl atoms and two N atoms from two symmetry-related bipy ligands in a distorted square-pyramidal geometry. The complex contains one-dimensional $\mathrm{Ag}^{\mathrm{I}}$–bipy chains, which are further linked by rarely formed T-frame $\mu_3$-Cl to form a two-dimensional bilayer structure.

## Comment

The design and synthesis of inorganic–organic composite coordination polymers exhibiting novel structures and properties have provided exciting new prospects (Blake, Brooks *et al.*, 1999; Blake, Champness *et al.*, 1999; Blake *et al.*, 2000; Evans & Lin, 2002; Kitagawa *et al.*, 2004; Yaghi *et al.*, 2003; Applegarth *et al.*, 2005). As an important class of metal–organic frameworks, hybrid organic–inorganic materials, especially metal halides, have attracted increasing attention (Engelhardt *et al.*, 1989; Zhang *et al.*, 2007, 2005). In recent years, some hybrid copper halides constructed by *N*-donor ligands have been reported (Graham *et al.*, 2000). However, to the best of our knowledge, Ag–*X* skeletons have rarely participated in constructing this kind of hybrid material, maybe due to the strong depositing trend of silver and halogens (Zhang *et al.*, 2008; Bowmaker *et al.*, 2005; Zartilas *et al.*, 2007). 4,4′-Bipyridine (bipy) and its analogues are neutral linear ligands widely used as excellent spacers in the construction of novel metal–organic compounds including diverse motifs (Wang *et al.*, 2007; Withersby *et al.*, 1997). Recently, we have undertaken a series of investigations into the assembly of $\mathrm{Ag}^{\mathrm{I}}$ cations with different angular and linear bipodal *N*-donor ligands, such as aminopyrimidine and aminopyrazine (Luo, Huang, Chen *et al.*, 2008; Luo, Huang, Zhang *et al.*, 2008; Luo *et al.*, 2009; Sun, Luo, Huang *et al.*, 2009; Sun, Luo, Xu *et al.*, 2009; Sun, Luo, Zhang *et al.*, 2009), with the principal aim of obtaining supramolecular compounds or ordered functional coordination polymers. In an attempt to exploit AgCl–*N*-donor hybrid materials under ammoniacal conditions, we successfully synthesized the title two-dimensional coordination polymer, (I), with (4,4) net topology.



(I)

Single-crystal X-ray diffraction study reveals that the asymmetric unit of (I) comprises one half of the chemical repeat unit shown in the scheme, where the Ag and Cl atoms lie on twofold axes, while the bipy ligands also sit across twofold axes. As shown in Fig. 1, the five-coordinated $\mathrm{Ag}^{\mathrm{I}}$ center adopts a slightly distorted square-pyramidal geometry, which is completed by three symmetry-related Cl atoms and two N atoms from two independent bipy ligands. The distortion of the $\mathrm{AgN}_2\mathrm{Cl}_3$ square pyramid is indicated by the calculated value of the $\tau$ factor (Addison *et al.*, 1984), which is 0.11 in (I) (for ideal square-pyramidal geometry, $\tau = 0$). The Ag—N bond length is 2.285 (3) Å, and one Ag—Cl bond length is 2.6802 (18) Å while the other two are 2.9797 (10) Å, which are within normal ranges (Turner *et al.*, 2005; Massoud & Langer, 2009; Oxtoby *et al.*, 2002; Fan *et al.*, 2007).

Coordination of one Cl atom to three or more Ag atoms is well-known, but in most examples described so far, the geometry consists of four Ag atoms and four Cl atoms occupying the apices of a cube, with *P*-donor ligands coordinated

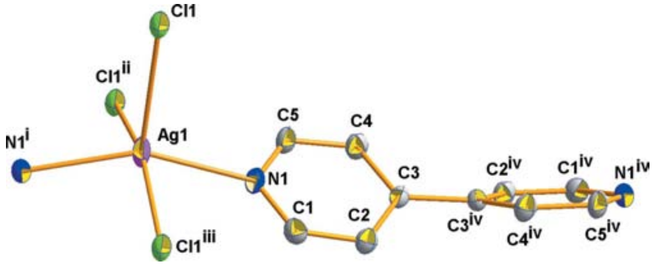


**Figure 1**
The coordination environment around the $\mathrm{Ag}^{\mathrm{I}}$ center in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z + 2$; (iv) $-x, y, -z + \frac{1}{2}$.]

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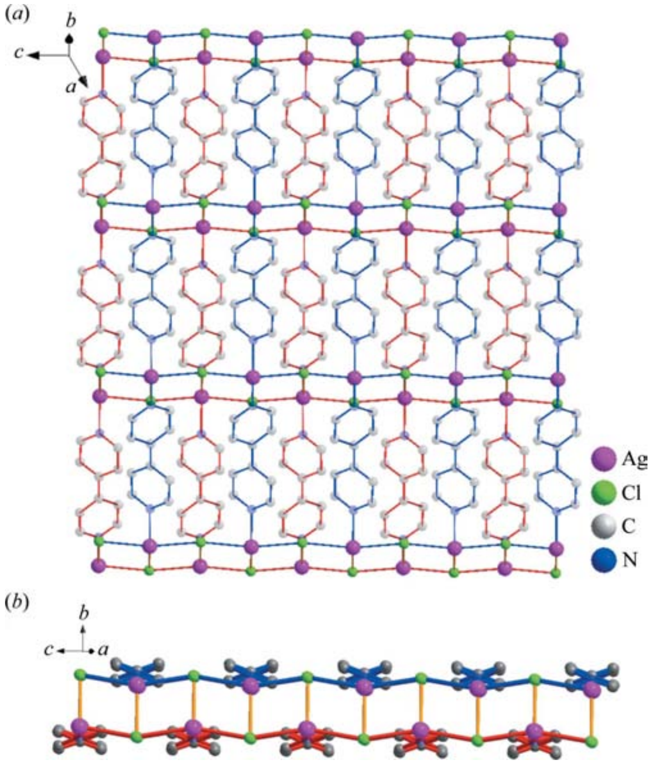

**Figure 2**
Schematic representations of the two-dimensional bilayer structure of (I), formed by the crosslinking of pairs of (4,4) nets, viewed along two different directions.

to the Ag centers (Bowen *et al.*, 1994; Zartilas *et al.*, 2009). The three $\mu_3$-Cl atoms and one Ag atom of (I) are coplanar, with maximum and minimum Cl—Ag—Cl angles of 160.94 (5) and 99.53 (3)°, respectively. This planar T-frame $\mu_3$-bridging mode of a Cl atom is still quite rare in AgCl-based hybrid materials (Blanco *et al.*, 2002).

The twofold-symmetric bipy ligand has a twisted nonplanar conformation, with a dihedral angle between the two pyridyl rings of 41.96 (3)°. The bipy ligand acts as an *N*:*N*′-bridging donor to link the $Ag^I$ cations into one-dimensional chains, within which the N—Ag—N angle is 154.11 (18)°. This deviates from the value of 180° for linear two-coordinated $Ag^I$ cations, due to the existence of the $\mu_3$-Cl atoms. The shortest Ag$\cdots$Ag distance is 3.6631 (12) Å, which is obviously longer than twice the van der Waals radius of silver(I) (1.72 Å; Bondi, 1964), indicating no direct metal–metal interaction between them.

In addition, as shown in Fig. 2, the Ag–bipy chains are further linked to form an ordered (4,4) net with the crystallographic dimensions of a rectangular subunit of 5.877 × 11.495 Å, in which $Ag^I$ is assigned to be a four-connected node. Adjacent pairs of layers are crosslinked through $\mu_3$-Cl atoms to form two-dimensional bilayers with a thickness of 2.680 Å, which is established by the separation distance between the Ag and Cl atoms. Furthermore, aromatic face-to-face contact between the pyridyl rings of adjacent bilayers remains a dominant supramolecular interaction in (I), with a centroid–centroid separation distance between the strictly parallel rings of 3.623 (3) Å (offset distance = 1.708 Å), and this extends the two-dimensional bilayer structure into a three-dimensional supramolecular framework and stabilizes the resulting molecular packing.

In conclusion, a new two-dimensional $Ag^I$ coordination polymer with a bipodal rigid spacer was successfully synthesized. It is constructed by single crosslinking (4,4) nets through Ag–Cl pillars and exhibits a rare T-frame Cl atom in a $\mu_3$-bridging mode.

## Experimental

All reagents and solvents were obtained commercially and used without further purification. AgCl (143 mg, 1 mmol) and 4,4′-bipyridine (156 mg, 1 mmol) were stirred in $CH_3OH$–$H_2O$ mixed solvent (10 ml, 1:1 *v*/*v*) for 30 min. Aqueous $NH_3$ solution (25%) was added dropwise until a clear solution was obtained. The formation of the product is not affected by changes in the reaction mole ratio of organic ligands to metal ions. The resultant solution was allowed to evaporate slowly in the dark at room temperature for several weeks to give colorless block-shaped crystals of (I). The crystals were isolated with deionized water and dried in air (yield *ca* 76%, based on Ag). Elemental analysis calculated for $C_{10}H_8AgClN_2$: C 40.10, H 2.69, N 9.35%; found: C 40.15, H. 2.73, N 9.28%.

### *Crystal data*

$[AgCl(C_{10}H_8N_2)]$
$M_r$ = 299.50
Monoclinic, $C2/c$
$a$ = 12.870 (4) Å
$b$ = 13.548 (4) Å
$c$ = 5.8772 (18) Å
$\beta$ = 116.729 (5)°
$V$ = 915.3 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.45 mm$^{-1}$
$T$ = 298 K
0.06 × 0.05 × 0.04 mm

### *Data collection*

Oxford Gemini S Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008) $T_{min}$ = 0.867, $T_{max}$ = 0.909
2362 measured reflections
910 independent reflections
891 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.063

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.090
$S$ = 1.22
910 reflections
65 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.97 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.84 e Å$^{-3}$

Aromatic H atoms were generated geometrically, with C—H = 0.93 Å, and allowed to ride on their parent atoms in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *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: KU3015). Services for accessing these data are described at the back of the journal.

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