

One-Dimensional Coordination Polymers of Silver(I) with Aminomethylpyridines. Example of a Triple Helical Infinite Chain

Sunkari Sailaja and M. V. Rajasekharan*

School of Chemistry, University of Hyderabad, Hyderabad-500 046, India

Received February 9, 2000

Crystal structures of the three isomeric compounds Ag(2-amp)ClO₄ (**1**), Ag(3-amp)ClO₄ (**2**), and Ag(4-amp)ClO₄ (**3**) reveal different packing arrangements of one-dimensional (1-D) infinite chain coordination polymers, formed in each case by the coordination of Ag to the pyridine N and amino N atoms from two different ligand molecules. **1**: triclinic, space group $P\bar{1}$, with $a = 7.672(6)$ Å, $b = 11.1401(11)$ Å, $c = 11.322(4)$ Å, $\alpha = 91.207(14)^\circ$, $\beta = 105.52(4)^\circ$, $\gamma = 90.48(2)^\circ$, and $Z = 2$. **2**: monoclinic, space group $P2_1/c$, with $a = 8.345(4)$ Å, $b = 8.6748(7)$ Å, $c = 26.056(9)$ Å, $\beta = 97.96(4)^\circ$, and $Z = 4$. **3**: hexagonal, space group $P6_522$, with $a = 9.3154(11)$ Å, $c = 39.313(5)$ Å, and $Z = 12$. **1** consists of zigzag chains, while **2** is made up of triple helical chains generating a tunnel space large enough to hold half the anions inside it. **3** has a highly symmetrical arrangement of 12 crystallographically equivalent chains held by weak Ag \cdots Ag bonds. The crystal packing of the 1-D polymers in this case may be described in terms of either helical ladders or stacked double layers.

Introduction

Coordination polymers form an important class of compounds with a potential for exhibiting unusual and desirable properties.¹ The design of such compounds takes into account the coordination characteristics (viz., geometrical and ligand atom preferences) of the metal ion as well as the structural features (viz., charge, multifunctionality, and chelate- and bridge-forming ability) of the ligand. We have recently demonstrated the formation of a polymeric chain of alternating eight-coordinate Ca²⁺ and 9-coordinate Ce⁴⁺ polyhedra using the multifunctional ligand dipicolinic acid, which can act as a chelating as well as a bridging ligand.² Ag⁺, on the other hand, has a preference for linear two-coordinate geometry and can serve to link bridging ligands to form polymeric chains. Crystal structures are sometimes influenced by Ag \cdots Ag interactions.³ The affinity of Ag⁺ for N-donor ligands, especially pyridine and its derivatives, is well-known. 2-Aminomethylpyridine (2-amp), which readily forms trischelates, is known to bind in the bridging mode in a few compounds.^{4,5} Its isomers 3-aminomethylpyridine (3-amp) and 4-aminomethylpyridine (4-amp) can only act as bridging ligands. In this paper we report three polymeric compounds of the type AgLClO₄ (L = 2-amp, 3-amp, or 4-amp), which serve to illustrate the profound changes in polymeric and crystalline structures caused by a simple variation of ligand structure.

Experimental Section

AgClO₄·H₂O was prepared according to a reported procedure.⁶ 2-amp, 3-amp, and 4-amp were purchased from Lancaster Chemicals.

Ag(2-amp)ClO₄ (1), Ag(3-amp)ClO₄ (2), and Ag(4-amp)ClO₄·0.5H₂O (3). In all cases white precipitates were obtained in near-quantitative yield by mixing aqueous solutions of silver(I) perchlorate and the ligand in a 1:1 molar ratio. In a typical experiment, 2-amp (1.20 mL, 11.6 mmol) was added to a solution of AgClO₄·H₂O (2.255 g, 10.01 mmol) in 5 mL of water and stirred for about 10–15 min. The white precipitate formed was filtered, washed with cold water, and dried. *Caution: Perchlorate salts are dangerous (especially if they are dry) and should be handled with care.* The complexes were crystallized by slow concentration of aqueous solutions over concentrated H₂SO₄ in a desiccator. In the case of **3**, the crystal structure analysis revealed half a molecule of lattice water per formula unit. Anal. Calcd for **1** (C₆H₈N₂O₄ClAg): C, 22.84; H, 2.56; N, 8.88. Found: C, 23.10; H, 2.54; N, 9.13. Anal. Calcd for **2** (C₆H₈N₂O₄ClAg): C, 22.84; H, 2.56; N, 8.88. Found: C, 23.03; H, 2.55; N, 8.11. Anal. Calcd for **3** (C₆H₉N₂O_{4.5}ClAg): C, 22.21; H, 2.80; N, 8.63. Found: C, 22.97; H, 2.43; N, 8.98. IR (KBr disk, cm⁻¹): for **1**, 3325(br), 1595, 1477, 1437, 1087(br), 761, 626; for **2**, 3344, 1595, 1483, 1431, 1087(br), 788, 625; for **3**, 3315(br), 1612, 1429, 1086(br), 806, 625.

X-ray Crystallography. X-ray data were collected using graphite-monochromated Mo K α radiation on an Enraf-Nonius CAD4 diffractometer for a crystal with dimensions of 0.46 × 0.40 × 0.28 mm for **1**, 0.76 × 0.24 × 0.16 mm for **2**, and 0.14 × 0.14 × 0.32 mm for **3**. An empirical absorption correction based on a ψ plot⁷ was applied to the intensity data. **1** belongs to the triclinic system, **2** to the monoclinic system, and **3** to the hexagonal system. The structures were solved (SHELXS-97⁸) and refined (over F^2 using SHELXL-97⁹) in the $P\bar{1}$ space group for **1**, $P2_1/c$ for **2**, and $P6_522$ for **3**. The ring hydrogens were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms. Methylene and amine hydrogen positions were located from difference maps, and bond length

- (1) Chen, C.-T.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293. Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, 283. Michaelides, A.; Skoulikis, S.; Kiritsis, V.; Aubry, A. *Chem. Commun.* **1995**, 1415. Kahn, O.; Martinez, C. J. *Science* **1998**, *279*, 44. Bertelli, M.; Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Mater. Chem.* **1997**, *7*, 1271.
- (2) Swarnabala, G.; Rajasekharan, M. V. *Inorg. Chem.* **1998**, *37*, 1483.
- (3) (a) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 1675. (b) Tong, M.-L.; Chen, X.-M.; Ye, B.-H.; Ng, S. W. *Inorg. Chem.* **1998**, *37*, 5278. (c) Robinson, F.; Zaworotko, M. *Chem. Commun.* **1995**, 2413. (d) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1996**, *118*, 295.
- (4) Crawford, C. A.; Day, E. F.; Streib, W. E.; Huffman, J. C.; Christou, G. *Polyhedron* **1994**, *13*, 2933.
- (5) Swarnabala, G.; Rajasekharan, M. V. *Polyhedron* **1997**, *16*, 921.

(6) Hill, A. E. *J. Am. Chem. Soc.* **1921**, *43*, 254.

(7) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351. Reibenspies, J. DATCOR program, 1989.

(8) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Germany, 1997.

(9) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Germany, 1997.

Table 1. Crystallographic Data

	1	2	3
empirical formula	C ₁₂ H ₁₆ Ag ₂ Cl ₂ N ₄ O ₈	C ₁₂ H ₁₆ Ag ₂ Cl ₂ N ₄ O ₈	C ₆ H ₈ AgClN ₂ O _{4.5}
fw	630.93	630.93	323.46
<i>a</i> (Å)	7.672(6)	8.345(4)	9.3154(11)
<i>b</i> (Å)	11.1401(11)	8.6748(7)	9.3154(11)
<i>c</i> (Å)	11.322(4)	26.056(9)	39.313(5)
α (deg)	91.207(14)	90	90
β (deg)	105.52(4)	97.96(4)	90
γ (deg)	90.48(2)	90	120
<i>V</i> (Å ³)	932.1(8)	1868.0(11)	2954.4(6)
<i>Z</i>	2	4	12
space group	<i>P</i> 1̄ (no.2)	<i>P</i> 2 ₁ / <i>c</i> (no.14)	<i>P</i> 6 ₅ 22 (no.179)
<i>T</i> (°C)	20	20	20
λ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm ⁻³)	2.248	2.243	2.182
μ (cm ⁻¹)	24.38	24.33	23.14
R1 ^a	0.0463	0.0600	0.0579
wR2 ^b	0.1130	0.1505	0.0981

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum (wF_o^4)]^{1/2}$. $w^{-1} = [\sigma^2(F_o^2) + (AP)^2 + BP]$. $P = (F_o^2 + 2F_c^2)/3$. $A = 0.0873$, $B = 0.01$ for **1**; $A = 0.0904$, $B = 6.25$ for **2**; $A = 0.0400$, $B = 4.34$ for **3**.

constraints were applied. The final R1 and wR2 values, respectively, were 0.0463 and 0.1130 for **1**, 0.0600 and 0.1505 for **2**, and 0.0579 and 0.0981 for **3**. Crystal data are given in Table 1, and selected bond lengths and angles and important noncovalent contacts are given in Table 2.

Table 2. Selected Bond Lengths (Å) and Angles (deg) and Important Noncovalent Contacts for **1**, **2**, and **3**^a

Ag(2-amp)ClO ₄ (1)			
Bond Distances			
Ag(1)–N(3)	2.160(3)	Ag(1)–N(2)	2.164(3)
Ag(2)–N(1)#1	2.153(3)	Ag(2)–N(4)	2.156(3)
Bond Angles			
N(3)–Ag(1)–N(2)	171.01(12)	N(1)#1–Ag(2)–N(4)	172.62(13)
Hydrogen Bonds ^b			
N(2)–HN2A···O(4)#3	2.06(3), 3.00(1), 156(4)		
N(2)–HN2B···O(1)	2.21(3), 3.16(1), 159(4)		
Ring–Ring Contacts			
C(11)···N(3)#4	3.55(1)		
Ag(3-amp)ClO ₄ (2)			
Bond Distances			
Ag(1)–N(1)	2.153(6)	Ag(2)–N(3)	2.172(6)
Ag(1)–N(4)	2.168(7)	Ag(2)–N(2)#1	2.177(7)
Bond Angles			
N(1)–Ag(1)–N(4)	179.4(3)	N(3)–Ag(2)–N(2)#1	169.1(2)
Hydrogen Bonds ^b			
N(2)–HN2A···O(3)	2.13(3), 3.21(1), 170(7)		
N(2)–HN2B···O(3)#4	2.35(7), 3.18(1), 132(7)		
N(4)–HN4A···O(6)	2.12(11), 3.17(2), 151(8)		
N(4)–HN4B···O(5)#5	2.44(12), 3.22(1), 148(10)		
Ring – Ring Contacts			
C(7)···C(1)#2	3.36(1)	C(9)···C(5)#2	3.57(1)
Ag(4-amp)ClO ₄ (3)			
Bond Distances			
Ag(1)–N(1)	2.149(9)	Ag(1)–N(2)#1	2.141(9)
Bond Angles			
N(2) #1–Ag(1)–N(1)	178.6(4)		
Hydrogen Bonds ^b			
N(2)–HN2A···O(5)	2.36(11), 2.97(2), 119(8)		
Ring – Ring Contacts			
N(1)···N(1)#2	3.27(1)	C(1)···N(1)#2	3.50(2)
C(1)···C(5)#2	3.53(2)	C(5)···N(1)#2	3.60(1)
Ag–Ag Contact			
Ag(1)···Ag(1)#2	3.38(2)		

^a Symmetry transformations used to generate equivalent atoms: For **1**, (#1) *x*, *y* + 1, *z*; (#3) $-x$, $-y$ + 1, $-z$; (#4) $-x$ + 1, $-y$ + 1, $-z$ + 1. For **2**, (#1) $-x$ + 1, *y* + 3/2, $-z$ + 1/2; (#2) *x*, *y* + 1, *z*; (#4) $-x$, *y* – 1/2, $-z$ + 1/2; (#5) $-x$ + 1, $-y$ + 2, $-z$. For **3**, (#1) *x*, *y* – 1, *z*; (#2) $-x$ + *y*, *y*, $-z$ + 3/2. ^b The sequence of numbers after each hydrogen bond are *d*(H···A), *d*(D–A), and \angle DHA, where A and D denote a H bond acceptor and donor, respectively.

Results

In all three complexes, the Ag atoms have nearly linear coordination with the pyridine and amine N atoms from two different ligands, resulting in polymeric chains. There is only very weak interaction between the Ag atoms and perchlorate O atoms (the shortest Ag···O distance is 2.732(3) Å). The perchlorate ions are involved in hydrogen bonding with the amino groups. The structure of Ag(2-amp)ClO₄ (**1**) is similar to that of the previously reported nitrate analogue,⁵ except that the two Ag(2-amp) moieties that form the repeating unit in **1** (Figure 1) are crystallographically different while in the nitrate salt they are related by symmetry. The crystal is made up of zigzag chains, with the perchlorate ions occupying the voids formed between centrosymmetrically related chains (Figure 2). The structures of Ag(3-amp)ClO₄ and Ag(4-amp)ClO₄, which have some unusual features, are described below.

The asymmetric unit of **2**, shown in Figure 3, consists of two Ag(3-amp)ClO₄ subunits. However, the polymeric chain is based on a repeating unit containing four Ag(3-amp) moieties. The chains assemble in the form of a triple helix (Figure 4). The helical repeat distance is 3 times the *b* axis translation. There are two enantiomeric triple helices running through the unit cell. This formation produces nearly 4 Å wide tunnels along the *b* axis. Half the ClO₄[–] ions are stacked inside these tunnels, while

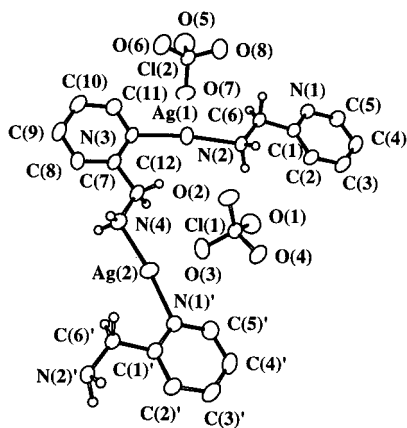


Figure 1. Structure of **1**. Atoms are represented by displacement ellipsoids at the 40% probability level. The prime denotes $x, y + 1, z$.

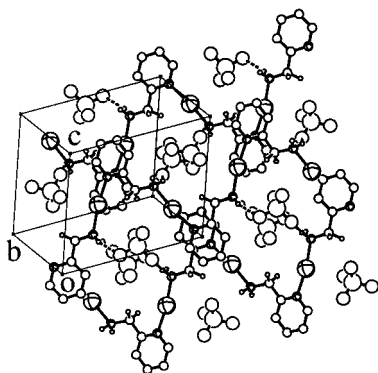


Figure 2. Packing diagram of **1**. Large "footballs" represent silver atoms, and small "footballs" represent nitrogen atoms. Chlorine atoms are represented by large open circles.

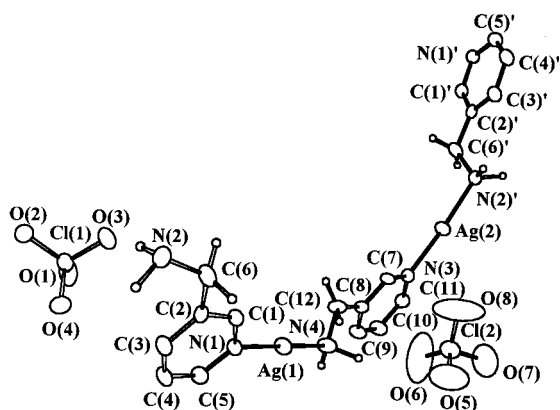


Figure 3. Structure of **2**. Atoms are represented by displacement ellipsoids at the 30% probability level. The prime denotes $-x + 1, y + 1.5, -z + 0.5$.

the other half are stacked outside (Figure 5). Another unusual feature of the structure is that each triple helix is "connected" by H bonding of the ClO_4^- oxygen atoms from within the helix to the NH_2 groups of the adjacent helix, leading to the formation of a H-bonded string of triple helices along the a axis (Figure 6).

The polymeric chain of **3** has just one $[\text{Ag}(4\text{-amp})]\text{ClO}_4$ in its repeating unit (Figure 7). As expected from the ligand structure, the polymeric chain is more linear in this case. It has, in fact, a sawtooth-like appearance due to the sharp bend at each $-\text{CH}_2$ group. There are 12 symmetry-related polymeric chains running through the crystallographic unit cell. Since all the chains run in the xy plane, the structure may be viewed as

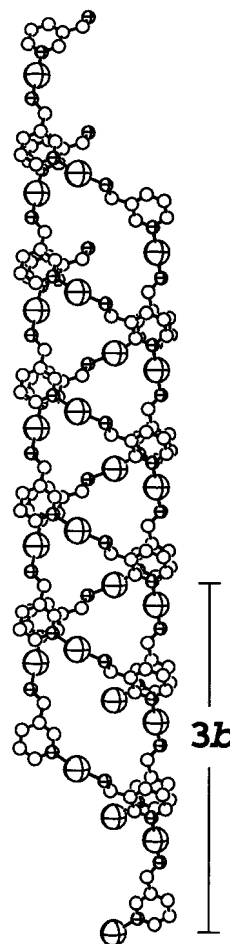


Figure 4. Triple helical polymer in **2** showing the helical repeat distance along the b axis.

made up of alternating layers of polymeric chains and cations (Figure 8). Lattice water is also found in the cation layer. The 6-fold screw symmetry causes the polymer chains to assemble in a helical fashion. The presence of the weak $\text{Ag}\cdots\text{Ag}$ bond gives the appearance of a ladder formation as shown in Figure 8a. However, there is no bond along the helix. Another description of the structure would be in terms of stacked double layers formed by two planes of linear polymers rotated by 60° and connected by $\text{Ag}\cdots\text{Ag}$ bonds. This aspect of the packing is illustrated in Figure 8b. Similar topologies for polymeric networks have been previously described.¹⁰

Discussion

Several helical coordination polymers are already known, even though they are less numerous than the (finite length) helicates.¹¹ Examples exist for single^{3b,12} and double¹³ helical infinite chains. In the case of double and higher order helices,

- (10) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1998**, 31 and references therein.
 (11) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, 97, 2005.
 (12) (a) Reddy, K. R.; Rajasekharan, M. V.; Tuchagues, J.-P. *Inorg. Chem.* **1998**, 37, 5978. (b) Kaes, C.; Hosseini, M. W.; Rickard, C. E. F.; Skelton, B. W.; White, A. H. *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 920. (c) Hester, C. A.; Baughman, R. G.; Collier, H. L. *Polyhedron* **1997**, 16, 2893. (d) Biradha, K.; Seward, C.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **1999**, 38, 492. (e) Suzuki, T.; Kotsuki, H.; Isobe, K.; Moriya, N.; Nakagawa, Y.; Ochi, M. *Inorg. Chem.* **1995**, 34, 530. (f) Batten, S. R.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 636. (g) Doyle, G. A.; Goodgame, D. M. L.; Sinden, A.; Williams, D. J. *Chem. Commun.* **1993**, 1170.

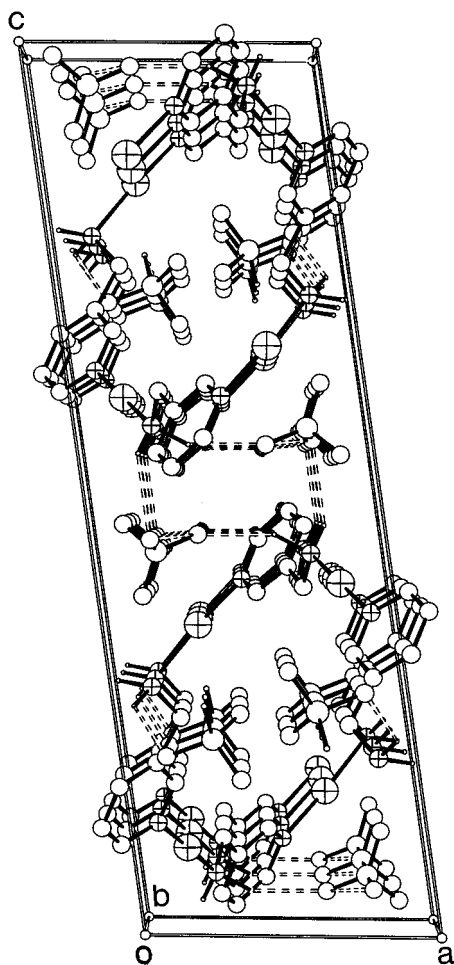


Figure 5. Packing diagram of **2** showing the packing of the perchlorate ions inside and outside the tunnels formed by the two enantiomeric helices in the unit cell. Hydrogen bonds are shown as broken lines.

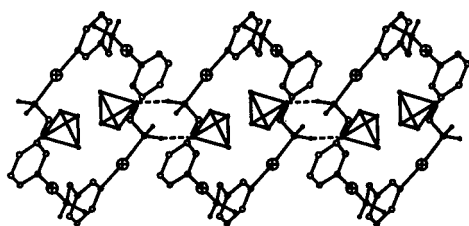


Figure 6. A view of the packing of **2** projected on the helix axis, showing the hydrogen bonds formed between the perchlorate ions (shown as tetrahedra) inside one helix and the “exo” amino hydrogens of the adjacent helix. These hydrogen bonds link together the helices along the *a* axis.

it is necessary to distinguish between two possibilities. (i) The strands of the helix are independent infinite chains held together by noncovalent forces other than the coordinate bond, quite analogous to the situation in DNA. This can be readily realized only for linear two-coordinate metal ions. $\text{Ag}(\text{CF}_3\text{SO}_3)\{1,3\text{-bis-(4-pyridyl)propane}\}^{13a}$ is a double helical complex of this type, where the two strands are held by $\text{Ag}\cdots\text{Ag}$ interaction. In another recent example of a double helix based on again a Ag(I) complex, the strands are held together by van der Waals interactions.^{13b} (ii) The strands are not independent, but are attached through coordinate bonds to a column of metal atoms

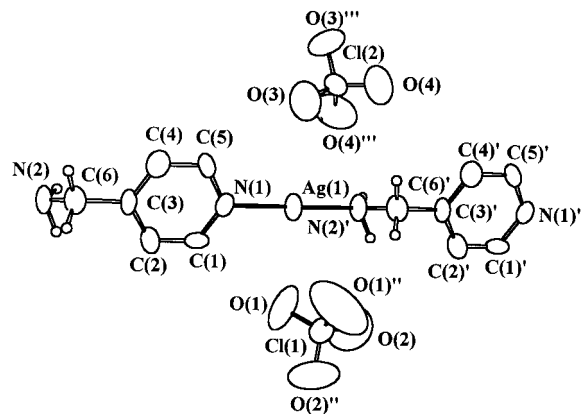


Figure 7. Structure of **3**. Atoms are represented by displacement ellipsoids at the 40% probability level. The single prime denotes $x, y - 1, z$, the double prime denotes $y, x, -z + 1.6667$, and the triple prime denotes $-x + y + 1, y, -z + 1.5$.

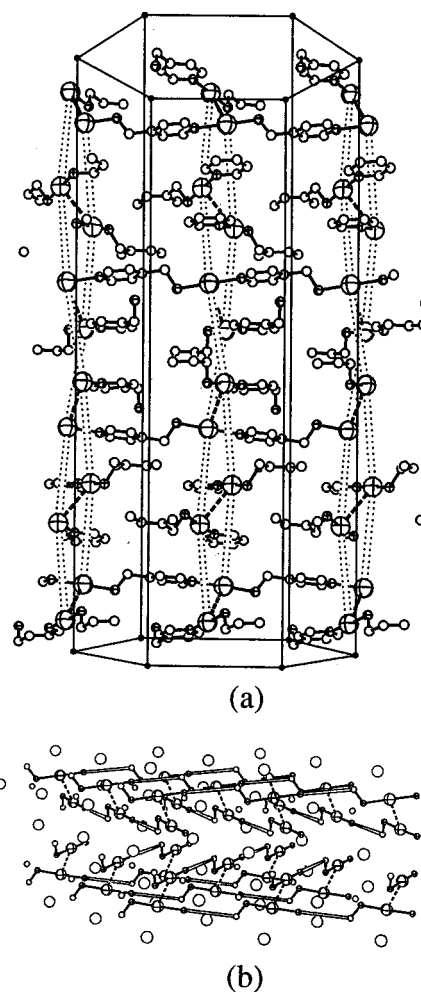


Figure 8. Two views of the crystal packing in **3**. (a) Arrangement of the symmetry-related polymeric chains in the hexagonal cell. The dashed bonds denote $\text{Ag}\cdots\text{Ag}$ long contacts. The dotted lines are drawn only as an aid for the eye to visualize the helical packing and do not represent chemical bonds. (b) Stacking of double layers viewed sideways to the hexagonal axis. The open circles represent the chlorine atoms of the perchlorate ions and lattice water molecules. The aromatic rings are reduced to double-line “bonds” connecting the nitrogen atoms, for clarity. $\text{Ag}\cdots\text{Ag}$ long contacts (dashed bonds) connect the two layers rotated by 60° with respect to each other.

(13) (a) Carlucci, L.; Ciani, G.; Gudenberg, D. W. v.; Proserpio, D. M. *Inorg. Chem.* **1997**, *36*, 3812. (b) Mamula, O.; Zelewsky, A. v.; Bark, T.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2945.

which form the axis of the helix.¹⁴ While there are no examples of true coordination polymers of this type, an interesting case

of a dinuclear Cu(I) complex which stacks together to give the appearance of an infinite double helix has been reported.¹⁵ To our knowledge, **2** is the first triple helical infinite chain coordination polymer, and it belongs to type i discussed above. The helical coil in **2** is unique in generating a tunnel space large enough to accommodate 50% of the anions.¹⁶ Since the repeat unit is made up of four complex moieties, when projected down its axis, the helix reduces to a squarate (in appearance) as shown in Figure 6. It is noteworthy that all the NH₂ groups are arranged on the outside of the "square". This *exo*-orientation of the NH₂ groups is complementary to the *endo*-orientation of the CH₂ groups. As a result, the anions within a helical coil will have to form H bonds only with the NH₂ groups of the adjacent coil. The volume of the tunnel space generated is almost the same for the alternative (*exo*-CH₂, *endo*-NH₂) arrangement, even though the shape of the space is modified. The main reason for preferring the former conformation appears to be that it allows the anions which are outside the tunnels also to participate in H bonding.

The packing of the sawtooth-type chains in **3** is highly unusual in that there are 12 symmetry-related polymers in the lattice. These chains are networked through Ag⁺⋯Ag⁺ interactions. Ag⁺⋯Ag⁺ contacts are made possible by the absence of any weak sideways interaction with the anions which are involved only in H bonding with the NH₂ groups. Another polymeric silver complex crystallizing in this uncommon space group (*P6₅22*

or the enantiomeric *P6₁22*) has been reported,¹⁷ viz., Ag(3,6-di(4-pyridyl)-1,2,4,5-tetrazine)(NO₃). However, the Ag⁺⋯Ag⁺ "bond" is absent in this structure, and the six symmetry-related chains are networked through weak Ag–O interactions involving the anions leading to a (pseudo) square planar coordination at each Ag atom.¹⁸

It is important to compare the nature of the stacking interaction between the aromatic rings in the three compounds. The packing in all three complexes permits significant π – π interaction (Table 2). However, it appears to be much more important in **2** and **3** and less so in **1**. In **1**, the interacting rings are strictly coplanar, though slipped, while in **2** and **3** they are inclined to each other by 10°.

Conclusion

The noncovalent interactions that govern the packing in the present series of polymeric compounds are H bonding, π – π interaction between the pyridine rings and Ag⁺⋯Ag⁺ interaction. The Ag remains strictly two-coordinate in **1** and **2**, while there is a weak Ag⁺⋯Ag⁺ bond in **3**. Since Ag–O bonds are absent, another factor responsible for the observed structures would be the (largely nondirectional) electrostatic interaction between the cationic chains and the tetrahedral anions. Helical structure in which the anions are packed inside as well as outside the coils or an alternating cation anion layer structure would lead to high electrostatic stabilization. The ligand structures of **2** and **3** appear to permit such packings without compromising on the other (directional) interactions.

Acknowledgment. We thank Prof. H. Stoeckli-Evans, University of Neuchatel, Switzerland, for helpful correspondence. We thank a reviewer for a helpful suggestion. This work was supported by the CSIR, New Delhi. The X-ray diffractometer was purchased using funds provided by the DST, New Delhi.

Supporting Information Available: One crystallographic file, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC000139A

- (14) The schematic of such an arrangement based on a dinuclear triple helicate has been discussed before. Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *Chem. Commun.* **1993**, 1019.
- (15) Carina, R. F.; Bernardinelli, G.; Williams, A. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1463.
- (16) However, networks of helices generating large cavities or tunnels are known. Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, *259*, 1596. See also ref 11d.
- (17) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327.
- (18) There are also two examples of helical coordination polymers crystallizing in this space group. See ref 11f,g.