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FULL PAPER

Syntheses, crystal structures and antimicrobial activities of polymeric silver(I) complexes with three amino-acids [aspartic acid (H_2asp), glycine (Hgly) and asparagine (Hasn)] †

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As model compounds for silver(I)–protein interactions, silver(I) complexes with three amino-acid ligands, *i.e.* aspartic acid (H_2asp), glycine (Hgly) and asparagine (Hasn), were prepared, characterized by elemental analysis, FTIR, TG/DTA, solution (^{1}H and ^{13}C) and solid-state (^{13}C and ^{15}N) NMR, and X-ray crystallography. Such complexes showed a wide spectrum of effective antimicrobial activities against Gram-negative (*E. coli*, *P. aeruginosa*) and -positive (*B. subtilis* and *S. aureus*) bacteria, yeasts (*C. albicans* and *S. cerevisiae*) and more than 11 tested molds. The crystal structures of four silver(I) complexes, $\{[Ag_2(\text{D-Hasp})(\text{L-Hasp})]\cdot 1.5H_2O\}_n$ **1**, $\{[Ag(gly)]_2\cdot H_2O\}_n$ **2**, $[Ag(\text{L-asn})]_n$ **3** and $[Ag(\text{D-asn})]_n$ **4**, were determined. The bonding modes of the silver(I) center were different for each complex, and different to those of the two recently reported silver(I) histidinates with only Ag–N bonds, *i.e.* water-soluble powder $[\{[Ag(Hhis)]\cdot 0.2EtOH\}_2]_n$ **6** and water-insoluble crystals $[Ag(Hhis)]_n$ **7**. Silver(I) complexes formed by amino-acids with N and O donor atoms and without an S atom can be classified into four types (I–IV) based on the bonding modes of the silver(I) center. Complex **1** belongs to type I which contains only Ag–O bonds, complex **2** belongs to type II, in which the two-coordinate O–Ag–O and N–Ag–N bonding units are alternately repeated, complexes **3** and **4** belong to type III, in which the two-coordinate N–Ag–O bonding units are repeated, and complexes that contain only Ag–N bonds, as recently found in the two silver(I) histidinates **6** and **7**, belong to type IV.

Introduction

In the bioinorganic chemistry of coinage metal(I) complexes there have been only a few biological and medicinal studies of silver(I) complexes, in contrast to the many studies on gold(I) complexes related to their antiarthritic,[1] antitumor,[1a,b,2] anti-HIV,[1a,b] and, recently, antimicrobial activities.[3] The studies of silver(I) complexes have been mostly related to their antiethylene[4] and antimicrobial activities.[3d–f,5] One recently highlighted topic in the coordination chemistry of coinage metal(I) atoms is the d^{10}–d^{10} interaction between two closed shell cations, or the metallophilic interaction, many examples of which have been reported in gold(I) and silver(I) complexes.[6–8] The aurophilic interaction, whose energy is similar to that of hydrogen bonds, has been rationalized by using relativistic and correlation effects.[6,7a] A second topic of interest is concerned with the helicity,[9] *i.e.* properties as helical polymers of d^{10} metals, most of which have been recently observed in silver(I) complexes such as single-stranded helices,[3e,9a,e,10a] double helix polymers[9d] and chiral helical polymers;[9b,f,10b,c] however, only a few such polymers have been observed in gold(I) complexes.[9g]

The mechanism of antimicrobial activity in silver(I) and gold(I) complexes has been scarcely reported, although three possible mechanisms for inhibition by the aqueous silver(I) ion have been proposed: (i) interference with electron transport, (ii) binding to DNA, and (iii) interaction with the cell membrane.[5a] Almost all of the silver(I)-PPh_3 complexes with $AgNP_2$, $AgNP_3$, $AgSP_2$ and $AgSP_3$ cores have shown no activity against bacteria, yeast or mold,[3e,f,10a,d,e] whereas the antimicrobial activities by the Ag–N, Ag–S and Ag–O bonding complexes without PPh_3 ligands depend upon the kind of coordinating donor atoms. For instance, the range of the antimicrobial activities observed in the Ag–S bonding compounds is narrower than that in the Ag–N bonding compounds such as $[Ag(im)]_n$ (Him = imidazole), $[Ag(1,2,4\text{-triz})]_n$ (Htriz = triazole), and $[Ag(tetz)]_n$ (Htetz = tetrazole).[10a,d] We have so far suggested that the coordination donor atoms to the silver(I) center and the ease of ligand replacement appear to be the key factors leading to a wide spectrum of antimicrobial activities, and the primary targets for the inhibition of bacteria and yeast by the silver(I) complexes are proteins as sulfur donor ligands, and not nucleic acids as N/O donors.[10d,e] This concept has been applied to the molecular design of silver(I) complexes showing a wide spectrum of effective antimicrobial activities. In fact, the polymeric silver(I) complexes with weaker bonds such as Ag–N and Ag–O bonds, *e.g.* $[\{[Ag(Hhis)]\cdot 0.2EtOH\}_2]_n$ **6** (H_2his = L-histidine; Ag_2N_4 core),[10b] $\{[Ag(Hpyrrld)]_2\}_n$ (H_2pyrrld = (*S*)-(−)- and (*R*)-(+)-2-pyrrolidone-5-carboxylic acid; Ag_2O_4 core)[10b,f] and $\{[Ag(othf)]_2\}_n$ (Hothf = (*S*)-(+)- and (*R*)-(−)-5-oxo-tetrahydrofurancarboxylic acid; Ag_2O_4 core),[10c] have been recently prepared and found to show a wider spectrum of effective antimicrobial activities. These facts have been considered to depend on whether or not the complexes can possess further ligand-replacement ability with the biological ligands.[10] The water-insoluble complex $[Ag(Hhis)]_n$ **7**,[10b] given with crystallization of water-soluble complex **6**, and the complexes $\{[Ag(S\text{-Hpyrrld})]_2\}_n$ and $\{[Ag(R\text{-Hpyrrld})]_2\}_n$,[10b,f] and the complexes $\{[Ag(S\text{-othf})]_2\}_n$ and $\{[Ag(R\text{-othf})]_2\}_n$[10c] were chiral helical polymers in the solid-state.

From the viewpoints of (1) model complexes for silver(I)–protein interaction, (2) the anticipated wider spectrum of antimicrobial activities and (3) structure–activity correlation, we focused on the silver(I) complexes of amino-acid ligands with both N and O donor atoms and without an S atom. However,

† Note: For ease of reference during discussion of their anions, H_2asp, Hgly and Hasn have been used as the abbreviations for the neutral amino-acids, rather than the conventional Asp, Gly and Asn, respectively.

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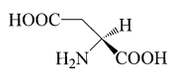
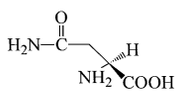
there are a limited number of silver(I) complexes for which X-ray structural analysis has been performed.[10b,11a–d] In this work, we prepared silver(I) complexes with three amino-acid ligands: aspartic acid (H_2asp), glycine (Hgly) and asparagine (Hasn), and characterized them by elemental analysis, thermogravimetric/differential thermal analysis (TG/DTA), FTIR, and solution (^{1}H and ^{13}C) and solid-state (^{13}C and ^{15}N) NMR spectroscopies, determined the crystal structures of $\{[Ag_2(\text{D-Hasp})(\text{L-Hasp})]\cdot 1.5H_2O\}_n$ **1**, $\{[Ag(gly)]_2\cdot H_2O\}_n$ **2**, $[Ag(\text{L-asn})]_n$ **3** and $[Ag(\text{D-asn})]_n$ **4**, and tested their antimicrobial activities against selected bacteria, yeasts and molds. The bonding modes of the silver(I) center in **1**–**4** are quite different from each other, and also different from those of the two recently reported silver(I) histidinates with only Ag–N bonds,[10b] *i.e.* water-soluble powder **6** and water-insoluble crystals **7**. The silver(I) complexes with amino-acid ligands with N and O donor atoms and without an S atom were classified into four types (I–IV) based on the bonding modes of the silver(I) center; type I with only Ag–O bonds, types II and III with both Ag–O and Ag–N bonds and type IV with only Ag–N bonds.



L-aspartic acid
(L-H_2asp)

H_2NCH_2COOH
glycine
(Hgly)



L-asparagine
(L-Hasn)

Herein we report full details of the synthesis of **1**–**4**, the crystal structures and their antimicrobial activities.

Results and discussion

Compositional characterization and properties

In the present synthesis, Ag_2O is used as the starting material of silver(I), but not $AgNO_3$ since we have found the starting $AgNO_3$ has sometimes caused contamination of the NO_3^- ion into the final product, which was difficult to remove. The complexes **1**–**4** were prepared from stoichiometric reactions of Ag_2O : ligand = 1 : 2 in aqueous media.

The molecular formulae and compositions of **1**–**4** were consistent with all data from the elemental analyses, TG/DTA, FTIR, solution (^{1}H and ^{13}C) and solid-state (^{13}C and ^{15}N) NMR spectra as shown in the Experimental section. By vapor diffusion at room temperature of an inner aqueous solution with an external organic solvent (EtOH for **1**, **2** and **4**, and acetone for **3**), complexes **1**, **2** and **4** were isolated in 77.0% (0.19 g scale), 39.8% (0.08 g scale) and 48.3% (0.11 g scale) yields, respectively, all as colorless needle crystals, but **3** was obtained in 54.6% (0.13 g scale) yield as colorless plate crystals. All complexes were sparingly soluble in water, but insoluble in organic solvents. Complexes **1**, **3** and **4** were light- and thermally-stable both in the solid-state and in aqueous solution, whereas **2** was unstable in aqueous solution to give a black suspension.

In **1** and **2**, the presence of 0.75 and 0.5 hydrated water molecules per silver, respectively, were confirmed from elemental analysis data and weight losses observed in TG/DTA measurements. On the other hand, **3** and **4** were isolated without any solvated molecules. Thermal analysis by TG/DTA measurements also showed that decompositions of **1**–**4** in the solid-state began around 171, 157, 164 and 170 °C, respectively.

The solid-state FTIR spectra showed that the carbonyl stretching bands of the two carboxyl groups of the coordinating $Hasp^-$ ligand in **1** appeared at 1600 cm^{-1} as a very intense and broad band, while those of the "free" H_2asp ligand were observed at 1693, 1646 and 1605 cm^{-1}. The 1600 cm^{-1} band in **1** shows that the two carboxyl groups in **1** are deprotonated, suggesting that the N_{amino} atom is protonated. As described later, single-crystal X-ray analysis has revealed that the dimeric silver(I) unit accomplished by coordination of the carboxyl oxygens of the $Hasp^-$ ligand forms a stair-like polymer by self-assembly *via* an interaction of the outside CO_2^- group with the silver(I) atom of the adjacent dimeric unit. The FTIR spectrum of **1** is consistent with the results of the single-crystal X-ray structure analysis. In **2**, the carbonyl stretching bands of the carboxyl group appeared at 1623 cm^{-1} as a shoulder band and at 1593 cm^{-1} as an intense and broad band, whereas those of the "free" Hgly ligand were observed at 1630 and 1596 cm^{-1}. The almost unchanged carbonyl stretching bands show that the carboxyl groups in **2** and the "free" Hgly ligand are deprotonated, reflecting the properties of the "free" ligand as a zwitterion. In **3**, the carbonyl stretching bands of the "free" Hasn ligand at 1681, 1649, 1611 and 1582 cm^{-1} were shifted to 1680, 1644 and 1577 cm^{-1} after the complexation. The carbonyl band of the terminal NH_2CO– group can be assigned to the unchanged 1681 cm^{-1} band, and, therefore, its group does not participate in coordination to the silver(I) center. The carboxyl group of the coordinating ligand is deprotonated and can interact significantly with the silver(I) center. This feature is also consistent with the results of the single-crystal X-ray structure analysis.

The ^{1}H NMR spectrum in D_2O of **1** showed the signals of the coordinating $Hasp^-$ ligand as two double doublets for the CH_2 group (H_a δ 2.67, H_b δ 2.82) and a double doublet (four lines) for the CH group (δ 3.90). The ^{13}C NMR in D_2O of **1** was a four-line spectrum consisting of the CH_2 group (δ 39.1), CH group (δ 54.8) and two carboxyl carbon signals (δ 176.8 and 180.0), each as a single peak, showing two $Hasp^-$ ligands in the dimeric units equivalent in solution. These chemical shifts were shifted from those of the "free" ligand in D_2O; ^{1}H NMR: H_a δ 2.93 and H_b δ 3.00 for the CH_2 group, and δ 4.04 for the CH group; ^{13}C NMR: δ 37.3 for the CH_2 group, δ 53.4 for the CH group, and δ 175.6 and 177.0 for two carboxyl groups. The ^{1}H NMR spectrum in D_2O of **2** showed a single peak for the CH_2 group (δ 3.39), and the ^{13}C NMR in D_2O showed two carbon resonances for the CH_2 (δ 47.8) and carboxyl groups (δ 180.1), all of which were shifted from the ^{1}H (δ 3.54) and ^{13}C (δ 44.0 and 174.7) resonances for the "free" ligand in D_2O. Although complex **2** is relatively unstable in aqueous solution, these spectra are probably due to the coordinating gly^- ligand in solution. The ^{1}H NMR spectrum in D_2O of **3** showed the signals of the coordinating asn^- ligand as two double doublets for the CH_2 group (H_a δ 2.59, H_b δ 2.82) and a double doublet (four lines) for the CH group (δ 3.78). The ^{13}C NMR in D_2O of **3** was a four-line spectrum consisting of the CH_2 group (δ 40.4), the CH group (δ 55.6) and two carboxyl carbon signals (δ 178.0 for NH_2CO, 179.2 for CO_2^-). All chemical shifts were shifted from those of the "free" ligand in D_2O; ^{1}H NMR: H_a δ 2.86 and H_b δ 2.96 for the CH_2 group and δ 4.01 for the CH group; ^{13}C NMR: δ 37.1 for CH_2, δ 53.8 for CH, and δ 175.7 and 176.8 for the NH_2CO and CO_2^- groups.

The solid-state ^{13}C NMR of **1** showed a three-line spectrum for the CH_2, CH and carboxyl groups at δ 37.8, 53.5 and 176.9, in contrast to a four-line spectrum for the "free" ligand at δ 35.4, 52.3, 175.0 and 178.1. It should be noted that the carboxyl carbon resonance of **1** was observed as a single peak at δ 176.9, as supported by X-ray crystallography. Since the solution ^{13}C NMR of **1** showed the carboxyl carbon resonance as two peaks at δ 176.8 and 180.0, this complex will probably be present as a bis(carboxylato-*O*,*O*′)-bridged dimer $[Ag_2(\text{D-Hasp})(\text{L-Hasp})]$ in aqueous solution, being different from its

self-assembling polymer in the solid-state. Similar behavior has been observed in the previously reported Ag_2O_4 core complex, $\{[Ag(Hpyrrld)]_2\}_n$.[10b,f] The solid-state ^{15}N NMR resonance of **1** at δ 21.8 was less influenced upon complexation ("free" ligand at δ 17.4), showing no coordination of the amino group.

In contrast, the solid-state ^{13}C NMR of **2** showed a two-line spectrum for the CH_2 and carboxyl group at δ 48.8 and 179.3, which were significantly shifted from those of the "free" ligand at δ 42.9 and 175.0, respectively. The solid-state ^{15}N NMR signal of **2** at δ −10.1 was significantly shifted upfield, compared with that of the "free" ligand at δ 12.3. The solid-state ^{13}C NMR of **3** was a four-line spectrum for the CH_2, CH, NH_2CO and carboxyl groups, at δ 40.9, 53.9, 177.7 and 178.9, respectively, each as a single peak, and these chemical shifts can be compared with those of the "free" ligand at δ 39.7, 56.2, 173.8 and 177.7, respectively. The solid-state ^{15}N NMR of **3**, consisting of a two-line spectrum for NH_2 and NH_2CO at δ 0.04 and 87.9, respectively, can be compared with those of the "free" ligand at δ 19.0 and 93.9, respectively. The ^{15}N NMR signal of the NH_2 group was much more shifted to upfield, suggesting that the NH_2 group participates in the coordination, but the NH_2CO group does not. These results are also supported by X-ray crystallography.

Crystal and molecular structures of 1–4

The molecular structures of complexes **1**–**3**, with the atom numbering schemes, are depicted in Figs. 1–3, respectively.

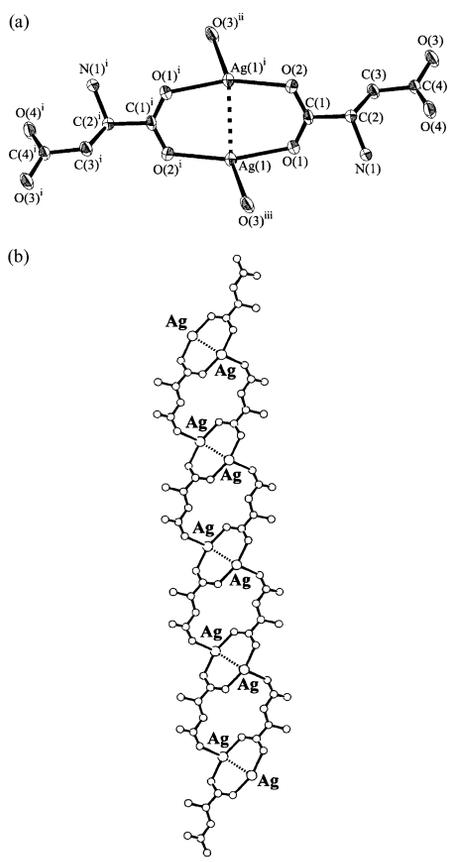


Fig. 1 (a) Molecular structure of the local coordination around silver(I) centers of $\{[Ag_2(D\text{-Hasp})(L\text{-Hasp})]\cdot 1.5H_2O\}_n$ **1** with 50% probability ellipsoids (symmetry operators: i $-x+2, -y, -z$; ii $x, y, z-1$; iii $-x+1, -y, -z+1$), and (b) side view of the stair-like, polymer chain extended across the crystallographic *a* and *c* axes.

Selected bond distances and angles, with their standard deviations, are given in Tables 1–4.

As shown in Fig. 1b, complex **1** is a stair-like polymer formed by self-assembly of bis(carboxylato-*O*,*O*′)-bridged centrosymmetric dimers [Ag_2(D-Hasp)(L-Hasp)], with the carboxylato

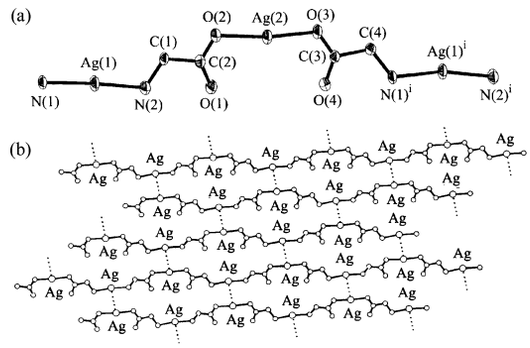


Fig. 2 (a) Molecular structure of the local coordination around silver(I) centers of $\{[Ag(gly)]_2\cdot H_2O\}_n$ **2** with 50% probability ellipsoids (symmetry operator: i $x-1.5, -y+0.5, z-0.5$), and (b) side view of the polymer chains extended along the crystallographic *a* axis.

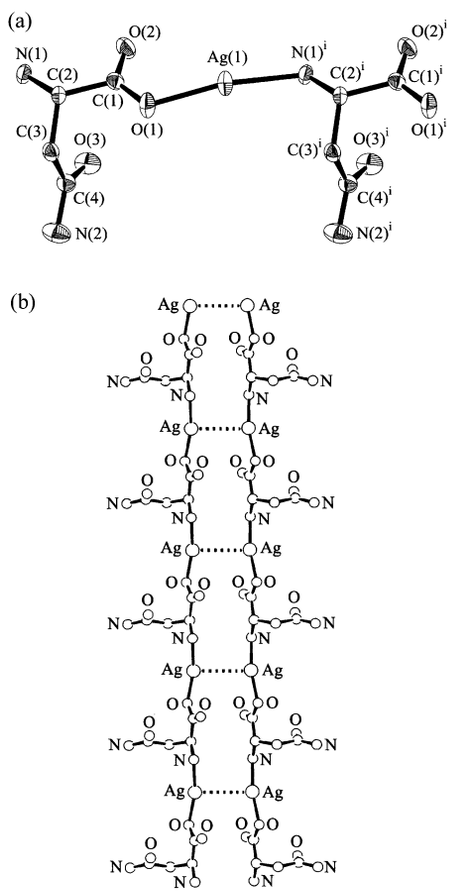


Fig. 3 (a) Molecular structure of the local coordination around silver(I) centers of $[Ag(L\text{-asn})]_n$ **3** with 50% probability ellipsoids (symmetry operator: i $x-1, y, z$), and (b) side view of the polymer chains extended along the crystallographic *a* axis.

group of the $Hasp^-$ ligand serving in the symmetric *syn–syn* bridging mode [C–O distances 1.243(6) and 1.260(6) Å, O–C–O angles 127.0(4)°; Fig. 1a, Table 1]. Of particular note is the fact that the Ag–Ag separation [2.8679(8) Å)] in the dimeric unit was slightly smaller than that in metallic silver (2.88 Å)[12a] and significantly less than twice the van der Waals radii for silver (3.44 Å),[12b] indicating the presence of an intramolecular metal–metal interaction.[8,10b] The intra-dimer Ag–O distances were Ag(1)–O(1) 2.234(3), Ag(1)–O(2)^i 2.223(3) Å and O(1)–Ag(1)–O(2)^i angle 161.1(1)°. The structure was extended into a stair-like polymer running across the crystallographic *a* and *c* axes *via* metal carboxylate linkage [Ag(1)–O(3)^{iii} distance 2.403(4) Å] between adjacent dimers, generating centrosymmetric Ag_2O_4 units. The solvated water molecules were located near the nitrogen atoms of amino groups. The FTIR spectrum of **1** also

Table 1 Selected bond distances (Å) and angles (°) for **1**

Ag(1) ··· Ag(1)^{i}	2.8679(8)	Ag(1)–O(1)	2.234(3)
Ag(1)–O(2)^{i}	2.223(3)	Ag(1)–O(3)^{iii}	2.403(4)
O(1)–C(1)	1.243(6)	O(2)–C(1)	1.260(6)
O(3)–C(4)	1.273(5)	O(4)–C(4)	1.237(5)
N(1)–C(2)	1.493(6)	C(1)–C(2)	1.530(6)
C(2)–C(3)	1.517(6)	C(3)–C(4)	1.523(6)
Ag(1)–Ag(1)^{i}–O(1)^{i}	80.27(9)	Ag(1)–Ag(1)^{i}–O(2)	82.90(9)
Ag(1)–Ag(1)^{i}–O(3)^{ii}	131.9(1)	O(1)–Ag(1)–O(2)^{i}	161.1(1)
O(1)–Ag(1)–O(3)^{iii}	86.8(1)	O(2)–Ag(1)^{i}–O(3)^{ii}	110.9(1)
Ag(1)–O(1)–C(1)	124.8(3)	Ag(1)^{i}–O(2)–C(1)	122.6(3)
O(1)–C(1)–O(2)	127.0(4)	O(1)–C(1)–C(2)	118.4(4)
O(2)–C(1)–C(2)	114.6(4)	N(1)–C(2)–C(1)	109.3(4)
N(1)–C(2)–C(3)	111.3(4)	C(1)–C(2)–C(3)	112.8(4)
C(2)–C(3)–C(4)	113.1(4)	O(3)–C(4)–O(4)	123.1(4)
O(3)–C(4)–C(3)	117.3(4)	O(4)–C(4)–C(3)	119.5(4)

Table 2 Selected bond distances (Å) and angles (°) for **2**

Ag(1)–N(1)	2.152(4)	Ag(1)–N(2)	2.147(4)
Ag(2)–O(2)	2.134(4)	Ag(2)–O(3)	2.115(4)
O(1)–C(2)	1.222(6)	O(2)–C(2)	1.275(6)
O(3)–C(3)	1.271(6)	O(4)–C(3)	1.238(6)
N(1)^{i}–C(4)	1.471(6)	N(2)–C(1)	1.455(6)
C(1)–C(2)	1.524(7)	C(3)–C(4)	1.520(7)
N(1)–Ag(1)–N(2)	168.2(2)	O(2)–Ag(2)–O(3)	171.7(2)
Ag(2)–O(2)–C(2)	116.9(3)	Ag(2)–O(3)–C(3)	120.0(3)
Ag(1)^{i}–N(1)^{i}–C(4)	119.0(3)	Ag(1)–N(2)–C(1)	114.3(3)
N(2)–C(1)–C(2)	115.1(4)	O(1)–C(2)–O(2)	126.2(5)
O(1)–C(2)–C(1)	120.1(4)	O(2)–C(2)–C(1)	113.7(4)
O(3)–C(3)–O(4)	126.0(4)	O(3)–C(3)–C(4)	114.1(4)
O(4)–C(3)–C(4)	119.8(4)	N(1)^{i}–C(4)–C(3)	115.0(4)

Table 3 Selected bond distances (Å) and angles (°) for **3**

Ag(1)–O(1)	2.103(2)	Ag(1)–N(1)^{i}	2.131(2)
O(1)–C(1)	1.284(3)	O(2)–C(1)	1.233(3)
O(3)–C(4)	1.238(4)	N(1)–C(2)	1.474(3)
N(2)–C(4)	1.336(4)	C(1)–C(2)	1.546(3)
C(2)–C(3)	1.510(4)	C(3)–C(4)	1.510(4)
O(1)–Ag(1)–N(1)^{i}	167.93(9)	Ag(1)–O(1)–C(1)	119.0(2)
Ag(1)–N(1)^{i}–C(2)^{i}	117.5(2)	O(1)–C(1)–O(2)	126.0(2)
O(1)–C(1)–C(2)	113.7(2)	O(2)–C(1)–C(2)	120.3(2)
N(1)–C(2)–C(1)	111.8(2)	N(1)–C(2)–C(3)	111.7(2)
C(1)–C(2)–C(3)	112.8(2)	C(2)–C(3)–C(4)	113.9(2)
O(3)–C(4)–N(2)	122.2(3)	O(3)–C(4)–C(3)	121.2(3)
N(2)–C(4)–C(3)	116.6(3)		

Table 4 Selected bond distances (Å) and angles (°) for **4**

Ag(1)–O(1)	2.106(3)	Ag(1)–N(1)^{i}	2.131(3)
O(1)–C(1)	1.276(5)	O(2)–C(1)	1.235(5)
O(3)–C(4)	1.243(5)	N(1)–C(2)	1.460(5)
N(2)–C(4)	1.329(5)	C(1)–C(2)	1.551(5)
C(2)–C(3)	1.512(5)	C(3)–C(4)	1.512(5)
O(1)–Ag(1)–N(1)^{i}	168.2(1)	Ag(1)–O(1)–C(1)	118.9(3)
Ag(1)–N(1)^{i}–C(2)^{i}	117.8(2)	O(1)–C(1)–O(2)	126.4(4)
O(1)–C(1)–C(2)	113.7(3)	O(2)–C(1)–C(2)	119.8(3)
N(1)–C(2)–C(1)	112.2(3)	N(1)–C(2)–C(3)	112.0(3)
C(1)–C(2)–C(3)	112.3(3)	C(2)–C(3)–C(4)	114.0(3)
O(3)–C(4)–N(2)	122.8(4)	O(3)–C(4)–C(3)	120.6(4)
N(2)–C(4)–C(3)	116.6(4)		

suggested that the N_{amino} atom is protonated, and is consistent with the feature that the two anionic carboxyl groups participate in the formation of the dimeric [Ag_2(D-Hasp)(L-Hasp)] unit and in their self-assembly.

The molecular structure of **1** is compared with those of the two centrosymmetric silver(I) carboxylate complexes of triethyl betaine ($Et_3N^+CH_2CO_2^-$; Et_3Bet);[11e] one is a discrete centrosymmetric dimer [$Ag_2(Et_3Bet)_2(NO_3)_2$] with the intra-dimer Ag–Ag distance 2.928(1) Å [intra-dimer Ag–O distances 2.162(3) and 2.207(3) Å; O–Ag–O angle 160.9(1)°; Ag–O (chelating nitrato group) distances 2.524(3) and 2.6919(3) Å] and the other is a stair-like cationic polymer $[Ag_2(Et_3Bet)_2]_n$-$(ClO_4)_{2n}$ based on bis(carboxylato-*O*,*O*′)-bridged centrosymmetric $Ag_2(Et_3Bet)_2$ dimers with the intra-dimer Ag–Ag distance 2.856(2) Å [intra-dimer Ag–O distances 2.222(4) and 2.232(4) Å; O–Ag–O angle 163.6(1)°], which runs parallel to the *a* axis *via* metal carboxylate linkage between adjacent dimers. The fundamental unit of **1** is also compared with that found in the dimeric complex $[Ag_2(C_9H_8NO_3)_2(H_2O)_2]\cdot 2H_2O$ ($C_9H_8NO_3$ = *N*-acetylanthranilato) which forms a discrete centrosymmetric bis-carboxylato-*O*,*O*′ dimer with the intra-dimer Ag–Ag distance 2.831(2) Å [intra-dimer Ag–O distances 2.185(2) and 2.207(3) Å; O–Ag–O angle 160.91(1)°].[11f] The centrosymmetric dimeric complexes formed by two carboxylates and two silver(I) ions have also been reported in the silver(I)-amino-acid complexes such as β-alaninatosilver(I) nitrate $[Ag_2(NH_3(CH_2)_2CO_2)_2](NO_3)_2$ [Ag–Ag distance 2.855(4) Å; Ag–O distances 2.198(19) and 2.210(19) Å; O–Ag–O angle 161.6(8)°],[11a,b] and glycylglycinatosilver(I) nitrate $[Ag_2(Hglygly)_2](NO_3)_2$ (Ag–Ag distance 2.92 Å; mean Ag–O distance 2.19 Å; O–Ag—O angle 160°).[11c]

Complex **1** can be also compared with the stair-like polymer complex $\{[Ag_2(R\text{-othf})(S\text{-othf})]\}_n$ formed by self-assembly of the centrosymmetric dimers [Ag–Ag separation 2.781(1) Å; Ag–O distances 2.178(3) and 2.250(3) Å; O–Ag–O angle 164.8(1)°],[10c] and the related complex $\{[Ag_2(R\text{-Hpyrrld})(S\text{-Hpyrrld})]\}_n$ with a polymer sheet structure formed by self-assembly of the centrosymmetric dimeric cores [Ag–Ag distance 2.875(2) Å; Ag–O distances 2.193(4) and 2.200(4) Å; O–Ag–O angle 163.1(2)°].[10f]

As shown in Fig. 2a, complex **2** is a helical polymer with a longer pitch (14.542 Å between one O–Ag–O unit and the next, 14.467 Å between one N–Ag–N unit and the next), in which alternate silver(I) ions are bound to two $O_{carboxyl}$ and two N_{amino} atoms, respectively, *i.e.* the O–Ag–O and N–Ag–N bonding units are alternately repeated [Ag–O distances 2.134(4) and 2.115(4) Å; Ag–N distances 2.152(4) and 2.147(4) Å; O–Ag–O and N–Ag–N angles are 171.7(2) and 168.2(2)°, respectively, Table 2]. These data are in accord with the previously reported data of silver(I) glycinate hydrate with the same composition (Ag–O distances 2.12 and 2.13 Å; mean Ag–N distance 2.15 Å; O–Ag–O angles 172°).[11c] The structure runs parallel to the *a* axis. One hydrated water molecule is positioned between two carboxyl oxygen atoms that do not coordinate to the silver(I) atom. Also, as shown in Fig. 2b, there are weak interactions between two polymer chains (inter-chain closest Ag–Ag separation between N–Ag–N and O–Ag–O units 3.241 Å). These factors will probably account for the significant deviation N–Ag–N and O–Ag–O angles from 180°.

In the polymeric silver(I) complex with L-asparagine **3**, each silver(I) ion was bound to the $O_{carboxyl}$ atom of one asn^- ligand and to the N_{amino} atom of another, *i.e.* the N–Ag–O bonding units were repeated as shown in Fig. 3a [Ag(1)–O(1) and Ag(1)–N(1)^{i} distances are 2.103(2) and 2.131(2) Å, respectively; O(1)–Ag(1)–N(1)^{i} angle 167.93(9)°, Table 3]. The terminal NH_2CO– group did not participate in coordination to the silver(I) center, as also shown in the FTIR and solid-state ^{15}N NMR spectra. This compound was a stair-like chiral polymer, but not a helical polymer. The structure runs parallel to the *a* axis (Fig. 3b). There are weak interactions between inter-chain Ag atoms (Ag–Ag separation 3.437 Å). It was also confirmed that the structure of the enantiomeric complex with D-asparagine **4** was a mirror image of that of **3** (see Table 4). Similar bonding modes have been reported in the polymeric silver(I) glycinate anhydride $[Ag(gly)]_n$ (Ag–O and Ag–N distances are 2.11 and 2.14 Å, respectively; N–Ag–O angle 177°)[11c] and the polymeric silver(I) α-alaninate $[Ag(\alpha\text{-ala})]_n$[11d] [Ag–O and Ag–N distances are 2.111(5) and 2.125(7) Å, respectively; O–Ag–N angle 180(8)°]. It has been reported that the two

Table 5 Classification of silver(I) complexes with amino-acid ligands with N and O donor atoms and without an S atom

Type (bonding mode)	Silver(I) complexes
I (only Ag–O bonding units)	$\{[Ag_2(D\text{-}Hasp)(L\text{-}Hasp)]\cdot 1.5H_2O\}_n$ **1**, $\{[Ag(\beta\text{-}ala)]NO_3\}_2$,[11a,b] $[Ag(Hglygly)]NO_3$[11c]
II (alternately repeated O–Ag–O and N–Ag–N bonding units)	$\{[Ag(gly)]_2\cdot H_2O\}_n$ **2**
III (repeated N–Ag–O bonding units)	$[Ag(L\text{-}asn)]_n$ **3**, $[Ag(D\text{-}asn)]_n$ **4**, $[Ag(gly)]_n$,[11c] $[Ag(\alpha\text{-}ala)]_n$[11d]
IV (only Ag–N bonding units)	$[\{[Ag(Hhis)]\cdot 0.2EtOH\}_2]_n$ **6**,[10b] $[Ag(L\text{-}Hhis)]_n$ **7** [10b]

silver(I) glycinate complexes, *i.e.* as hydrate and anhydride, crystallize, often from the same solution, under basic conditions.[11c]

Classification of silver(I) complexes with amino-acid ligands

From the X-ray structure analysis, the silver(I) complexes with amino-acids with N and O donor atoms and without an S atom can be classified into four types (I–IV) based on the bonding modes of the silver(I) center; type I with only Ag–O bonds, types II and III with both Ag–O and Ag–N bonds and type IV with only Ag–N bonds (Table 5).

From the structural viewpoint, complex **1** belongs to type I, in which the silver(I) atoms coordinate to only carboxyl oxygen atoms to form Ag_2(carboxylato-O,O')$_2$ units. The Ag–N bonds are not contained. The silver(I) complexes $\{[Ag(\beta\text{-ala})]NO_3\}_2$[11a,b] and $[Ag(Hglygly)]NO_3$[11c] belong to this class. Related complexes, $[Ag_2(Et_3Bet)_2(NO_3)_2]$ and $[Ag_2(Et_3Bet)_2]_n(ClO_4)_{2n}$,[11e] also belong to this class.

The structure of polymeric silver(I) glycinate hydrate **2** belongs to type II, in which alternate silver(I) ions are bound to two $O_{carboxyl}$ and two N_{amino} atoms, respectively, *i.e.* the two-coordinate O–Ag–O and N–Ag–N bonding units are alternately repeated. Other examples of this type have not been found.

The polymeric silver(I) complexes with L- and D-asparagine, **3** and **4**, respectively, belong to type III, in which each silver(I) ion is bound to the $O_{carboxyl}$ atom of one asn$^-$ ligand and to the N_{amino} atom of another, *i.e.* the two-coordinate N–Ag–O bonding units are repeated. The polymeric silver(I) glycinate anhydride $[Ag(gly)]_n$[11c] and the polymeric silver(I) α-alaninate $[Ag(\alpha\text{-ala})]_n$[11d] also belong to this class.

The structure of silver(I) L-histidinate **7** as water-insoluble crystals belongs to type IV. X-Ray crystallography has revealed that **7** is a left-handed helical polymer consisting of a bent, two-coordinate silver(I) atom bonding to the N_{amino} atom of one Hhis$^-$ ligand and the N_π atom of a different Hhis$^-$ ligand, in which $O_{carboxyl}$ atoms do not participate in the coordination.[10b] The silver(I) L-histidinate **6** as a water-soluble powder in the solid-state is a polymer formed by intermolecular hydrogen bonding interactions between dimeric $[Ag(Hhis)]_2$ cores, in which N_π and N_{amino} atoms in two Hhis$^-$ ligands coordinate to two silver(I) atoms.[10b] The bonding modes of **6** and **7** are unique because $O_{carboxyl}$ atoms do not participate in the coordination.

Antimicrobial activities

Antimicrobial activities of the silver(I) complexes **1**–**4**, together with the results of the related complexes as a comparison, are listed in Table 6, as estimated by the minimum inhibitory concentration (MIC; μg mL^{-1}).

Antimicrobial activities of the "free" amino-acid ligands, D- and L-H_2asp, Hgly and D- and L-Hasn were estimated as > 1000 μg mL^{-1} for bacteria, yeast and mold, and thus showed no activity. As previously shown,[10a,d] the Ag^+ ion, as aqueous $AgNO_3$, showed remarkable activity against Gram-negative bacteria (*E. coli, P. aeruginosa*), moderate activity against Gram-positive bacteria (*B. subtilis*) and no activity against yeast and mold.

Interestingly, **1**–**4** and related complexes (types I–IV) showed a wide spectrum of effective activities against Gram-negative (*E. coli, P. aeruginosa*) and -positive (*B. subtilis* and *S. aureus*) bacteria and yeasts (*C. albicans* and *S. cerevisiae*), and even against more than 11 tested molds. It is concluded that all silver(I)-amino-acid complexes tested here, including the recently reported silver(I) histidinates **6** and **7**,[10b] show a wide spectrum of effective antibacterial and antifungal activities. As a matter of fact, the antimicrobial activities are in contrast to those of Ag–S bonding complexes and many phosphinesilver(I) complexes with $AgNP_2$, $AgNP_3$, $AgSP_2$ and $AgSP_3$ cores.[3e–g,10] The silver(I) complexes with D-, L- and DL-aspartic acid ligands showed the same antimicrobial activities. This is the case for the silver(I) complexes with D-, L- and D,L-asparagine ligands. Thus, these results primarily indicate that, rather than solubility, charge and chirality of the complexes, the type of coordination donor atom attached to the silver(I) center, namely, the weaker Ag–O and Ag–N bonding properties, play a key role in the wide spectrum of antimicrobial activities observed. These facts are also consistent with the recent results of the water-soluble Ag–O bonding silver(I) complexes, *i.e.* the polymeric silver(I) complexes, $\{[Ag(S\text{-Hpyrrld})]_2\}_n$,[10b] $\{[Ag(R\text{-Hpyrrld})]_2\}_n$,[10f] $\{[Ag_2(R\text{-Hpyrrld})(S\text{-Hpyrrld})]\}_n$,[10f] $\{[Ag(S\text{-othf})]_2\}_n$,[10c] $\{[Ag(R\text{-othf})]_2\}_n$,[10c] and $\{[Ag_2(R\text{-othf})(S\text{-othf})]\}$[10c] formed by self-assembly of the Ag_2(carboxylato-O,O')$_2$ units. The factor of the coordination donor atom, *i.e.* the ease of ligand replacement of silver(I) complexes, has been attributed to the fact that further ligand replacement with biological ligands is possible.[10] On the other hand, the difference in the magnitude of antimicrobial activity may come from the structural factor of the silver(I) complexes.

Conclusion

Polymeric silver(I) complexes with amino-acid ligands with N and O donor atoms and without an S atom such as DL-H_2asp, Hgly, and L- and D-Hasn, *i.e.* **1**–**4**, were prepared, characterized and their crystal structures determined by X-ray crystallography. They were classified into four types (I–IV) based on the bonding modes of the silver(I) center. All of the silver(I) amino-acid complexes showed a wide spectrum of effective antibacterial and antifungal activities, as found in the recent silver(I) histidinates **6** and **7**.[10b] The kind of coordination donor atom to the silver(I) center, namely, the weaker Ag–O and Ag–N bonding properties, play a key role, rather than the solubility, charge and chirality of the complexes. On the other hand, the difference in the magnitude of antimicrobial activity may come from the structural factor of the silver(I) complexes. From the viewpoint of the recent d^{10} metal chemistry, **1** was concerned with the metallophilic interaction, **2** with the helical polymer with longer pitch, and **3** and **4** with the chiral polymers. The title complexes are also of interest as a possible new type of solid-state inorganic polymer.

Experimental

Materials

D- and DL-aspartic acid (H_2asp), D- and L-asparagine (Hasn) (Aldrich); L-H_2asp (Nacalai Tesque); glycine (Hgly), DL-Hasn, Ag_2O, EtOH, diethyl ether, acetone (Wako); D_2O (99.9 D atom %) (Isotec) were reagent grade and used as received.

Table 6 Antimicrobial activities of silver(I) complexes evaluated by minimum inhibitory concentration (MIC; μg mL^{-1})

Microbe	L-H_2asp	{[Ag_2-(D-Hasp)-(L-Hasp)]·1.5H_2O}$_n$ **1**	{[Ag-(L-Hasp)]$_2$}$_n$	{[Ag-(D-Hasp)]$_2$}$_n$	Hgly	{[Ag(gly)]$_2$·H_2O}$_n$ **2**	L-Hasn	[Ag-(L-asn)]$_n$ **3**	[Ag-(D-asn)]$_n$ **4**	[Ag_2-(D-asn)-(L-asn)]$_n$ **5**
Escherichia coli	>1000	125	125	62.5	>1000	62.5	>1000	31.3	31.3	31.3
Bacillus subtilis	>1000	250	125	125	>1000	125	>1000	250	125	125
Staphylococcus aureus		250	125	125		62.5		250	125	125
Pseudomonas aeruginosa		125	125	62.5		62.5		62.5	31.3	31.3
Candida albicans		62.5	31.3	31.3		15.7		125	31.3	31.3
Saccharomyces cerevisiae		62.5	31.3	31.3		15.7		62.5	15.7	15.7
Aspergillus niger		62.5	62.5	62.5		31.3		62.5	62.5	62.5
Penicillium citrinum		62.5	62.5	62.5		62.5		62.5	62.5	31.3
Aspergillus terreus		62.5	31.3	31.3		31.3		125	62.5	62.5
Rhizopus stolonifer		125	62.5	31.3		62.5		125	31.3	31.3
Chaetomium globosum		62.5	31.3	31.3		15.7		15.7	15.7	15.7
Cladosporium cladosporioides		62.5	31.3	15.7		15.7		31.3	31.3	31.3
Penicillium islandicum		62.5	31.3	31.3		15.7		62.5	31.3	31.3
Aureobasidium pullulans		62.5	31.3	31.3		15.7		62.5	31.3	31.3
Fusarium moniliforme		62.5	31.3	31.3		15.7		125	62.5	125
Eurotium tonophilum		31.3	31.3	15.7		7.9				
Cladosporium sphaerospermum		31.3	31.3	15.7		15.7				

Instrumentation/analytical procedures

CHN elemental analyses were performed using a Perkin-Elmer PE2400 series II CHNS/O Analyzer (Kanagawa University). Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a Rigaku TG 8101D and TAS 300 data processing system. TG/DTA measurements were run under air with a temperature ramp of 4 °C min^{-1} between 30 and 500 °C. Infrared spectra were recorded on a Jasco FT-IR 300 spectrometer in KBr disks at room temperature.

^{1}H NMR (399.65 MHz) and ^{13}C{^{1}H} NMR (100.40 MHz) in solution were recorded in 5 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data processing system. ^{1}H NMR (500.00 MHz) and ^{13}C{^{1}H} NMR (125.00 MHz) in solution were also recorded on a JEOL JNM-ECP 500 FT-NMR spectrometer with a JEOL ECP-500 NMR data processing system. ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes were measured in D_2O solution with reference to an internal DSS or TSP. Chemical shifts are reported on the δ scale and resonances downfield of DSS or TSP (δ 0) are recorded as positive.

Solid-state ^{13}C NMR (75.58 MHz) and ^{15}N NMR (30.46 MHz) spectra were measured using a JEOL JNM-ECP 300WB FT-NMR spectrometer equipped with a cross-polarization (CP)/magic angle spinning (MAS) accessory. The ^{13}C and ^{15}N NMR spectral widths were 30.2 and 30.5 kHz, respectively. The ^{13}C and ^{15}N NMR spectra were accumulated 700–2000 and 11000–16000 times, respectively. The ^{13}C and ^{15}N NMR chemical shifts were calibrated indirectly through external hexamethylbenzene [17.3 ppm relative to TMS (δ 0)] and directly through external NH_4Cl (δ 0)‡, respectively. The experimental errors of the isotropic ^{13}C and ^{15}N NMR chemical shift values were estimated to be about 0.5 and 0.4 ppm, respectively.

Synthesis

{[Ag_2(D-Hasp)(L-Hasp)]·1.5H_2O}$_n$ 1. To a stirred suspension of 0.116 g (0.50 mmol) of Ag_2O in 30 mL water was added 0.133 g (1.00 mmol) of solid DL-H_2asp. During 2 h stirring, the black suspension changed to an almost clear and colorless solution. Unreacted Ag_2O was filtered off by passing through a membrane filter (JV 0.1 μm). Vapor diffusion at room temperature using the colorless filtrate as an inner solution and 150 mL of EtOH as an external solvent was performed. After five days, colorless needle crystals formed, which were collected on a membrane filter (JG 0.2 μm), washed twice with 50 mL each of EtOH and ether, and dried *in vacuo* for 2 h. The clear colorless needle crystals obtained in 0.19 g (77.0%) yield were light- and thermally-stable, and sparingly soluble in water, but insoluble in most organic solvents {Found: C, 19.18; H, 2.69; N, 5.62. Calc. for $C_8H_{15}N_2O_{9.5}Ag_2$ or [Ag(Hasp)]$_2$·1.5H_2O: C, 18.95; H, 2.98; N, 5.53%}. TG/DTA data: weight loss of 5.18% was observed before decomposition; calc. 5.33% for x = 1.5 in [Ag(Hasp)]$_2$·xH_2O. Decomposition began around 171 °C with an endothermic peak at 102 °C and exothermic peaks at 182 and 335 °C. Prominent IR bands in the 1800–400 cm^{-1} region (KBr disk): 1600vs, 1487s, 1393s, 1353m, 1308m, 1230w, 1147w, 1108w, 1066w, 987m, 900w, 850w, 817w, 660m, 531m cm^{-1}. ^{1}H NMR (D_2O, 23.3 °C): δ 2.67 (H_a, dd, J 9.0, 8.5 Hz), 2.82 (H_b, dd, J 3.7, 13.7 Hz), 3.90 (1H, dd, CH, J 3.7, 5.4 Hz). ^{13}C NMR (D_2O, 25.3 °C): δ 39.1 (CH_2), 54.8 (CH), 176.8 (carboxyl), 180.0 (carboxyl). Solid-state ^{13}C CPMAS NMR (23.2 °C): δ 37.8 (CH_2), 53.5 (CH), 176.9 (carboxyl). Solid-state ^{15}N CPMAS NMR (23.2 °C): δ 21.8 (NH_2).

In the present synthesis, when L- and D-H_2asp ligands were used, {[Ag(L-Hasp)]$_2$}$_n$ and {[Ag(D-Hasp)]$_2$}$_n$ were obtained in 0.16 g (67.0%) and 0.17 g (69.4%) yields, respectively. However, the crystals obtained were of poor quality and not suitable for X-ray analysis.

{[Ag(gly)]$_2$·H_2O}$_n$ 2. To a stirred suspension of 0.116 g (0.50 mmol) of Ag_2O in 15 mL water was added a colorless solution of 0.075 g (1.00 mmol) of Hgly in 15 mL water. After 2 h stirring a black suspension, unreacted Ag_2O, was filtered off by passing through a membrane filter (JV 0.1 μm). In the dark, vapor diffusion at room temperature using the colorless filtrate as an inner solution and 150 mL of EtOH as an external solvent was performed. After three days, colorless needle crystals formed, which were collected on a membrane filter (JG 0.2 μm), washed twice with 50 mL each of EtOH and ether, and dried *in vacuo* for 2 h. The clear colorless needle crystals obtained in 0.08 g (39.8%) yield were sparingly soluble in water, but insoluble in most organic solvents. This compound was unstable in

‡ The solid-state ^{15}N NMR measurements of the previously reported silver(I) complexes [{[Ag(Hhis)]·0.2EtOH}$_2$]$_n$ **6**, [Ag(Hhis)]$_n$ **7** and {[Ag-(*S*-Hpyrrld)]$_2$}$_n$ were carried out with reference to external NH_4NO_3 (NH_4: δ 0).[10b] The ^{15}N NMR chemical shift of NH_4Cl was observed at δ 18 with reference to NH_4NO_3.

Table 7 Crystallographic data for **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_8H_{15}N_2O_{9.5}Ag_2$	$C_4H_{10}N_2O_5Ag_2$	$C_4H_7N_2O_3Ag$	$C_4H_7N_2O_3Ag$
Formula weight	506.95	381.87	238.98	238.98
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$C222_1$ (no. 20)	$C222_1$ (no. 20)
a/Å	5.6255(6)	8.905(2)	7.4245(9)	7.422(2)
b/Å	22.469(2)	6.404(2)	8.019(2)	8.011(3)
c/Å	5.6114(6)	15.355(1)	21.537(5)	21.526(3)
β/°	100.766(9)	97.86(1)		
V/Å^3	696.8(1)	867.4(3)	1282.2(4)	1279.9(4)
Z	2	4	8	8
μ/cm^{-1}	28.53	44.94	30.78	30.83
R_{int}	0.032	0.025	0.017	0.000
R	0.029	0.033	0.023	0.017
R_w	0.037	0.043	0.024	0.028

aqueous solution to give a black suspension {Found: C, 12.76; H, 2.34; N, 7.29. Calc. for $C_4H_{10}N_2O_5Ag_2$ or [Ag (gly)]$_2$·H_2O: C, 12.58; H, 2.64; N, 7.34%}. TG/DTA data: weight loss of 4.65% was observed before decomposition; calc. 4.72% for x = 1 in [Ag(gly)]$_2$·xH_2O. Decomposition began around 157 °C with an endothermic peak at 86 °C and exothermic peaks at 157 and 359 °C. Prominent IR bands in the 1800–400 cm^{-1} region (KBr disk): 1623vs, 1593vs, 1496s, 1402s, 1335m, 1301s, 1157w, 1128w, 1043m, 930m, 893m, 828m, 687m, 637m, 507m cm^{-1}. ^{1}H NMR (D_2O, 20.4 °C): δ 3.39 (2H, s, CH_2). ^{13}C NMR (D_2O, 21.6 °C): δ 47.8 (CH_2), 180.1 (carboxyl). Solid-state ^{13}C CPMAS NMR (23.9 °C): δ 48.8 (CH_2), 179.3 (carboxyl). Solid-state ^{15}N CPMAS NMR (23.6 °C): δ −10.1 (NH_2).

[Ag(L-asn)]$_n$ 3. To a stirred suspension of 0.116 g (0.50 mmol) of Ag_2O in 30 mL water was added 0.132 g (1.00 mmol) of solid L-Hasn. During 2 h stirring the black suspension changed to an almost colorless solution. Unreacted Ag_2O was filtered off by passing through a membrane filter (JV 0.1 μm). Vapor diffusion at room temperature using the colorless filtrate as an inner solution and 150 mL of acetone as an external solvent was performed. After five days, colorless plate crystals formed, which were collected on a membrane filter (JG 0.2 μm), washed twice with 50 mL each of acetone and ether, and dried *in vacuo* for 2 h. The clear colorless plate crystals obtained in 0.13 g (54.6%) yield were light- and thermally-stable, and sparingly soluble in water, but insoluble in most organic solvents {Found: C, 19.97; H, 2.79; N, 11.77. Calc. for $C_4H_7N_2O_3Ag$ or [Ag (L-asn)]: C, 20.10; H, 2.95; N, 11.72%}. TG/DTA data: no weight loss was observed before decomposition. Decomposition began around 164 °C with exothermic peaks at 177 and 386 °C. Prominent IR bands in the 1800–400 cm^{-1} region (KBr disk): 1680vs, 1644vs, 1577vs, 1529s, 1430m, 1401m, 1362m, 1314m, 1237w, 1150m, 1104w, 1075w, 887w, 807w, 669m, 518w cm^{-1}. ^{1}H NMR (D_2O, 21.3 °C): δ 2.59 (H_a, dd, J 8.8, 6.6 Hz), 2.82 (H_b, dd, J 4.2, 11.5 Hz), 3.78 (1H, dd, CH, J 4.2, 4.6 Hz). ^{13}C NMR (D_2O, 21.6 °C): δ 40.4 (CH_2), 55.6 (CH), 178.0 (NH_2CO), 179.2 (carboxyl). Solid-state ^{13}C CPMAS NMR (23.6 °C): δ 40.9 (CH_2), 53.9 (CH), 177.7 (NH_2CO), 178.9 (carboxyl). Solid-state ^{15}N CPMAS NMR (23.4 °C) [repeat trial at 24.1 °C]: δ 0.04 [−2.0] (NH_2), 87.9 [88.0] (NH_2CO).

In the synthesis, when D-Hasn was used and vapor diffusion with EtOH as an external solvent was carried out, colorless needle crystals of [Ag(D-asn)]$_n$ **4** were obtained in 0.11 g (48.3%) yield. ^{13}C NMR (D_2O, 24.4 °C): δ 39.8 (CH_2), 55.2 (CH), 177.6 (NH_2CO), 178.5 (carboxyl). Solid-state ^{13}C CPMAS NMR (24.0 °C): δ 40.9 (CH_2), 53.5 (CH), 176.1 (NH_2CO), 178.5 (carboxyl). Solid-state ^{15}N CPMAS NMR (23.7 °C): δ −0.08 (NH_2), 88.4 (NH_2CO). When vapor diffusion with acetone as an external solvent was performed, colorless plate crystals were obtained. Both crystals provided identical crystal structures. When DL-Hasn was used, {[Ag_2(L-asn)(D-asn)]}$_n$ **5** was obtained in 0.11 g (47.7%) yield.

X-Ray crystallography

Complexes **1**, **2** and **4** were obtained as colorless needle crystals and complex **3** as colorless plate crystals by vapor diffusion of internal aqueous solutions with an external organic solvent (EtOH for **1**, **2** and **4**, acetone for **3**). Each single-crystal of **1**, **3** and **4** was mounted on a glass fiber and that of **2** was sealed in a glass capillary, and used for measurements at room temperature of precise cell constants and intensity data collection on a Rigaku AFC5S diffractometer (Mo-Kα radiation, λ = 0.71069 Å). The structures were solved by direct methods followed by subsequent difference Fourier calculations and refined by a full-matrix least-squares procedure using the TEXSAN package.[13] All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Crystal data, data collection and structure refinement details for **1**–**4** are summarized in Table 7.

CCDC reference numbers 178114, 178115, 178154 and 178155.

See http://www.rsc.org/suppdata/dt/b2/b200684g/ for crystallographic data in CIF or other electronic format.

Antimicrobial activity

Antimicrobial activities of silver(I) complexes were estimated by the minimum inhibitory concentration (MIC: μg mL^{-1}) as described elsewhere.[10]

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