

# Water-soluble silver(I) complexes of (R)-(+)- and (S)-(-)-2-pyrrolidone-5-carboxylic acid and their antimicrobial activities. Chiral helical polymer and polymer sheet structures in the solid-state formed by self-assembly of dimeric [Ag(Hpyrrld)]<sub>2</sub> cores

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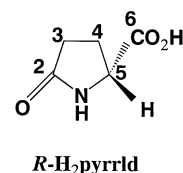
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The synthesis and characterization of two water-soluble silver(I) complexes {[Ag(R-Hpyrrld)]<sub>2</sub>}<sub>n</sub> **1** and {[Ag<sub>2</sub>(R-Hpyrrld)(S-Hpyrrld)]<sub>2</sub>}<sub>n</sub> **2** [R- and S-H<sub>2</sub>pyrrld = (R)-(+)- and (S)-(-)-2-pyrrolidone-5-carboxylic acid, respectively] showing wide ranging effective antimicrobial activity are described and their crystal structures determined. Single-crystal X-ray analysis reveals that **1** and **2** in the solid state are a right-handed chiral helical polymer and an achiral polymer sheet, respectively, formed by self-assembly of the Ag<sub>2</sub>(carboxylato-*O,O'*)<sub>2</sub> units [Ag–Ag 2.899(2) Å for **1** and 2.875(2) Å for **2**; O–Ag–O 160.3(5), 163.2(5)° for **1** and 163.1(2)° for **2**]. The helicity of **1** in the solid state was accomplished by connection of only one oxo group in one dimeric core to one of the silver(I) centers of the adjacent dimeric unit. It is elucidated that the chiral helical polymer **1** is a mirror image of the recently characterized enantiomer {[Ag(S-Hpyrrld)]<sub>2</sub>}<sub>n</sub> **3**. The bonding modes of **1** and **3** are quite different from those of the achiral polymer sheet **2**. Complexes **1** and **2** have been also characterized by elemental analysis, TG/DTA, FT-IR, and solution (<sup>1</sup>H and <sup>13</sup>C) and solid-state <sup>13</sup>C NMR spectroscopies. The wide ranging effective antimicrobial activities observed in the complexes suggest that weak silver(I)–oxygen bonding properties play a key role.

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

Recently, a water-soluble silver(I) complex {[Ag(S-Hpyrrld)]<sub>2</sub>}<sub>n</sub> **3** [S-H<sub>2</sub>pyrrld = (S)-(-)-2-pyrrolidone-5-carboxylic acid] showing wide ranging effective antimicrobial activity, which shows both a metallophilic interaction and helicity in the solid state, has been synthesized.<sup>10b</sup> This compound in the solid state is a left-handed chiral helical polymer formed by self-assembly of non-centrosymmetric bis-carboxylato-bridged disilver(I) units with an intramolecular Ag–Ag interaction [2.9022(7) Å], whereas it is present as a dimeric complex [Ag(S-Hpyrrld)]<sub>2</sub> in aqueous solution. The related, right- and left-handed chiral helical polymers {[Ag(R-othf)]<sub>2</sub>}<sub>n</sub> **4** and {[Ag(S-othf)]<sub>2</sub>}<sub>n</sub> **5**, respectively, and the stair-like polymer {[Ag<sub>2</sub>(R-othf)(S-othf)]<sub>2</sub>}<sub>n</sub> **6** [R- and S-Hothf ligands are (R)-(-)- and (S)-(+)-5-oxo-2-tetrahydrofuran-3-carboxylic

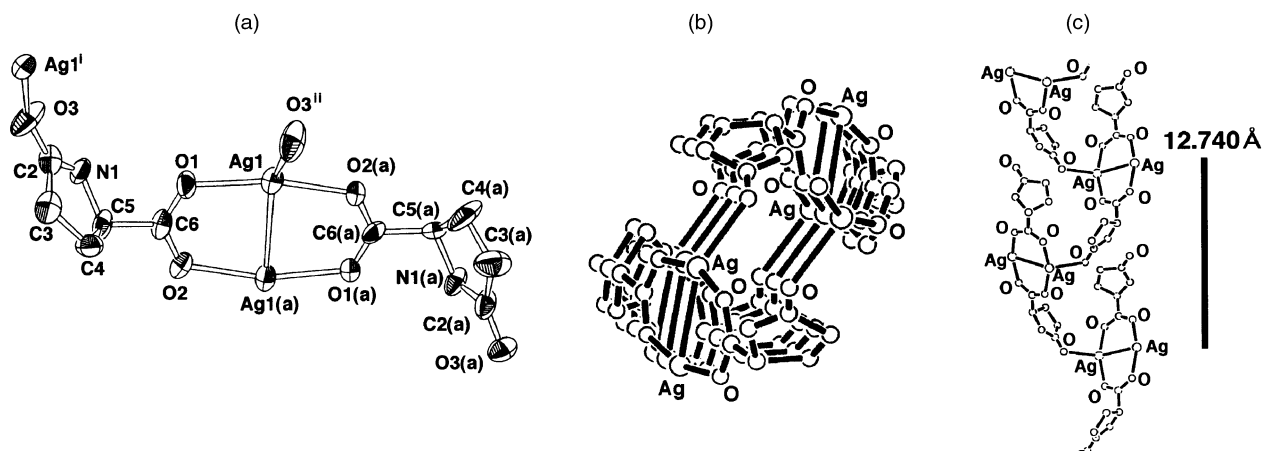
acid, respectively, in which the ring NH group in H<sub>2</sub>pyrrld is replaced with an oxygen atom] have been also prepared.<sup>10c</sup> Complexes **4** and **5** formed by self-assembly of [Ag(othf)]<sub>2</sub> cores, but the mode of self-assembly is different from that of **6** and, also, of **3**. Such differences have aroused our interest in the mode of self-assembly of such Ag<sub>2</sub>(carboxylato-*O,O'*)<sub>2</sub> units. Herein, using enantiomeric (R) and racemic (R,S) forms of the S-H<sub>2</sub>pyrrld ligand, the two water-soluble silver(I) complexes {[Ag(R-Hpyrrld)]<sub>2</sub>}<sub>n</sub> **1** [R-H<sub>2</sub>pyrrld = (R)-(+)-2-pyrrolidone-5-carboxylic acid] and {[Ag<sub>2</sub>(R-Hpyrrld)(S-Hpyrrld)]<sub>2</sub>}<sub>n</sub> **2** were synthesized and characterized by elemental analysis, thermogravimetric/differential thermal analyses (TG/DTA), FT-IR, and solution (<sup>1</sup>H and <sup>13</sup>C) and solid-state <sup>13</sup>C NMR spectroscopies. Their crystal structures were determined and their antimicrobial activities were also tested.



## Results and discussion

### Compositional characterization, and solution and solid-state NMR spectroscopies

Complexes **1** and **2** were prepared from stoichiometric reactions of Ag<sub>2</sub>O and H<sub>2</sub>pyrrld in a 1 : 2 mol ratio. The formulae of {[Ag(R-Hpyrrld)]<sub>2</sub>}<sub>n</sub> **1** and {[Ag<sub>2</sub>(R-Hpyrrld)(S-Hpyrrld)]<sub>2</sub>}<sub>n</sub> **2** were consistent with all data (elemental analysis, TG/DTA, FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra) shown in the Experimental section. These complexes were isolated without any solvated molecules.



**Fig. 1** (a) Molecular structure of the local coordination around silver(I) centers of **1** with 50% probability ellipsoids (symmetry operation i  $-x, y + 0.5, -z$ ; ii  $-x, y - 0.5, -z$ ). (b) Top view of the main axis showing approximate two-fold helical symmetry of the structure and (c) side view of the right-handed helical polymer chain extended along the crystallographic  $b$  axis with a pitch of 12.740 Å.

Thermal analysis by TG/DTA measurements showed that decomposition of **1** in the solid-state began around 182 °C, while that of **2** began around 170 °C.

The solid-state FT-IR spectra of **1** and **2** showed that the multiple vibrational bands in the region 3100–2600  $\text{cm}^{-1}$  observed in the “free” H<sub>2</sub>pyrrld ligand disappeared, and one very intense vibrational band around 3400  $\text{cm}^{-1}$  appeared after complexation. The carbonyl stretching bands of the “free” ligand at 1720 and 1648  $\text{cm}^{-1}$  were shifted to 1676 and 1593  $\text{cm}^{-1}$  after the complexation. These observations suggest that the peptide  $-\text{C}(\text{O})\text{NH}-$  bond in the ring is likely maintained in **1** and **2**, *i.e.*, the keto form of the ligand participates in the coordination, and the two carboxyl oxygen atoms accomplish the formation of the dimeric silver(I) unit. This feature is also consistent with the results of X-ray crystallography.

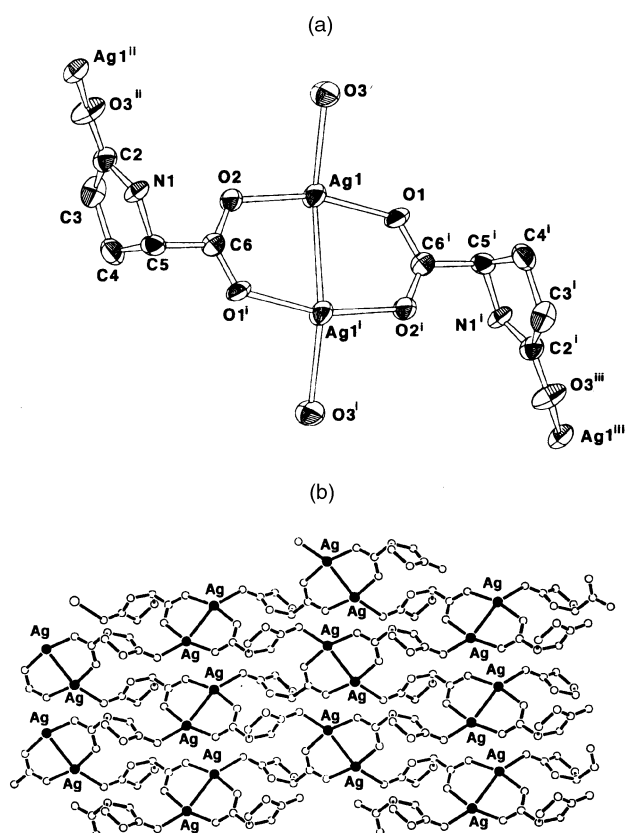
The  $^1\text{H}$  NMR spectra in D<sub>2</sub>O of **1** and **2** showed signals of the coordinating Hpyrrld<sup>−</sup> ligand as multiplet peaks for the two methylene groups (H4 and H3) and a double doublet (four lines) of the H5 proton within the ring. The  $^{13}\text{C}$  NMR spectra in D<sub>2</sub>O of **1** and **2** consisted of five lines arising from signals from C4, C3, C5, C6 and C2, each as a single peak, indicating that the two Hpyrrld<sup>−</sup> ligands in the dimeric units are equivalent in solution. Solid-state IR, and solution ( $^1\text{H}$  and  $^{13}\text{C}$ ) NMR spectra of **1** and **2** in D<sub>2</sub>O are very similar to each other, and to those of **3**. Complex **3** has been established as a dimer in aqueous solution by positive-ion electrospray ionization (ESI) mass spectrometry, solution ( $^1\text{H}$  and  $^{13}\text{C}$ ) NMR and solid-state ( $^{13}\text{C}$  and  $^{15}\text{N}$ ) NMR spectroscopies.<sup>10b</sup> Complexes **1** and **2** are also probably present as dimers in aqueous solution.

Solid-state  $^{13}\text{C}$  NMR signals of C2, C3 and C6 in **1** were observed as two peaks each, respectively, reflecting the presence of two inequivalent Hpyrrld<sup>−</sup> ligands in the solid state, as substantiated by X-ray crystallography. These results are consistent with those of **3**.<sup>10b</sup> On the other hand, the solid-state  $^{13}\text{C}$  NMR spectrum of **2** showed single peaks for C4, C3, C5, C6 and C2, suggesting that the two Hpyrrld<sup>−</sup> ligands are equivalent in the solid state. These results are also supported by X-ray crystallography.

### Crystal and molecular structures

Single crystals suitable for single-crystal X-ray analysis were obtained for **1** and **2**. Their molecular structures with the atom numbering schemes are depicted in Figs. 1 and 2, respectively. Selected bond distances and angles with their estimated standard deviations are given in Table 1.

As shown in Fig. 1(b) and (c), the crystal structure of **1** is an unusual single-stranded helical polymer, a 2<sub>1</sub> helix, composed of bis(carboxylato- $O,O'$ )-bridged  $[\text{Ag}(\text{R-Hpyrrld})]_2$  units, with



**Fig. 2** (a) Molecular structure of the local coordination around silver(I) centers of **2** with 50% probability ellipsoids (symmetry operation i  $-x + 1, -y, -z + 1$ ; ii  $-x + 0.5, y - 0.5, -z + 1.5$ ; iii  $x + 0.5, -y + 0.5, z - 0.5$ ). (b) Side view of the polymer sheet structure.

the carboxylato group acting in a *syn-syn* bridging mode [C–O 1.26(2), 1.28(2), 1.23(2), 1.24(2) Å; O–C–O 126(2), 130(2)°]. This polymer is formed by self-assembly of dimeric units [Fig. 1(a)]. The crystal structure consisted of the packing of right-handed 2-fold single helices, with a period along the crystallographic  $b$  axis, *i.e.*, a pitch of 12.740 Å. The helicity of **1** in the solid state was accomplished with a connection of only one ring carbonyl oxygen (O3) of one dimeric unit to one of the silver(I) centers (Ag1') of the adjacent dimeric unit [O3–Ag1' 2.46(1) Å]. The chiral helical polymer **1**, as a mirror image of **3**, is constructed with the chiral *R*-Hpyrrld<sup>−</sup> ligand.

The Ag–Ag separation [2.899(2) Å] in the dimeric unit of **1** [Fig. 1(a)] is close to that of metallic silver (2.88 Å)<sup>11a</sup> and

**Table 1** Selected bond distances (Å) and angles (°) for **1** and **2**

<b>1</b>		<b>2</b>	
Ag1–Ag1(a)	2.899(2)	Ag1–Ag1 <sup>i</sup>	2.875(2)
Ag1–O1	2.20(1)	Ag1–O1	2.193(4)
Ag1–O2(a)	2.19(1)	Ag1–O2	2.200(4)
Ag1(a)–O2	2.25(1)	O1–C6	1.259(7)
Ag1(a)–O1(a)	2.16(1)	O2–C6	1.247(8)
O1–C6	1.26(2)	O3 <sup>ii</sup> –C2	1.239(7)
O2–C6	1.28(2)	N1–C2	1.322(8)
O3–C2	1.22(2)	N1–C5	1.452(7)
O1(a)–C6(a)	1.23(2)	Ag1–O3	2.476(5)
O2(a)–C6(a)	1.24(2)		
O3(a)–C2(a)	1.23(2)		
N1–C2	1.33(2)		
N1–C5	1.47(2)		
N1(a)–C2(a)	1.36(2)		
N1(a)–C5(a)	1.46(2)		
Ag1 <sup>i</sup> –O3	2.46(1)		
O1–Ag1–O2(a)	160.3(5)	O1–Ag1–O	163.1(2)
O1(a)–Ag1(a)–O2	163.2(5)	O1–Ag1–O3	103.5(2)
Ag1–Ag1(a)–O2	79.5(3)	O1–Ag1–O3	91.5(2)
Ag1(a)–Ag1(a)–O2(a)	78.5(3)	Ag1 <sup>i</sup> –Ag1–O2	84.0(1)
Ag1–Ag1(a)–O1(a)	83.9(3)	Ag1 <sup>i</sup> –Ag1–O1	79.2(1)
Ag1(a)–Ag1–O1	83.5(3)	Ag1 <sup>i</sup> –Ag1–O3	148.4(1)
Ag1–O1–C6	123(1)	Ag1–O1–C6 <sup>i</sup>	128.5(4)
Ag1(a)–O1(a)–C6(a)	121(1)	Ag1–O2–C6	122.2(4)
Ag1–O2(a)–C6(a)	127(1)	Ag1 <sup>ii</sup> –O3 <sup>ii</sup> –C2	125.3(5)
Ag1(a)–O2–C6	126(1)	O1–C6–O2	126.1(6)
O1–C6–O2	126(2)		
O1(a)–C6(a)–O2(a)	130(2)		

significantly less than twice the van der Waals radii for silver (3.44 Å),<sup>11b</sup> indicating the presence of an intramolecular metal–metal interaction.<sup>8</sup> The Ag–Ag distances have been recently found to be significantly influenced by the softness of the coordinating donor atoms.<sup>10b</sup> The two silver(I) centers with different coordination numbers, *i.e.*, the non-centrosymmetric dimeric units of **1** [Ag–O 2.20(1), 2.19(1), 2.25(1), 2.16(1) Å; O–Ag–O 160.3(5), 163.2(5)°] can be compared with those of **3** [Ag–Ag 2.9022(7); C–O 1.226(8), 1.248(7), 1.252(8), 1.251(8) Å; Ag–O 2.188(5), 2.217(5), 2.220(4), 2.186(5) Å; O–C–O 126.8(6), 126.4(6)°, O–Ag–O 158.7(2), 163.6(2)°].<sup>10b</sup>

On the other hand, the crystal structure of **2** is a polymer sheet [Fig. 2(b)], composed of racemic [Ag<sub>2</sub>(*R*-Hpyrrld)(*S*-Hpyrrld)] units, with the carboxylato group acting in the *syn-anti* bridging mode [C–O 1.259(7), 1.247(8) Å; O–C–O 126.1(6)°]. This polymer sheet is also formed by self-assembly of the dimeric units, both ring carbonyl oxygens (O3<sup>ii</sup> and O3<sup>iii</sup>) of which participate in the coordination to the different silver(I) atoms (Ag1<sup>ii</sup> and Ag1<sup>iii</sup>). This bonding mode is in contrast to those of **1** and **3**. The O3<sup>ii</sup>–Ag1<sup>ii</sup> distance [2.476(5) Å] in **2** [Fig. 2(a)] is similar to those in **1** and **3** [2.46(1) and 2.470(4) Å, respectively]. The Ag–Ag separation [2.875(2) Å] is slightly shorter than those of **1** and **3**. The two silver(I) centers have the same coordination number and the dimeric units are centrosymmetric [Ag–O 2.193(4), 2.200(4) Å; O–Ag–O 163.1(2)°].

The chiral helical polymers **1** and **3** can be compared with related, chiral helical polymers of silver(I) complexes, {[Ag(*R*-othf)]<sub>2</sub>}<sub>n</sub> **4** and {[Ag(*S*-othf)]<sub>2</sub>}<sub>n</sub> **5** with almost the same pitch (5.417 and 5.416 Å, respectively).<sup>10c</sup> Both **4** and **5** have also been formed by self-assembly of non-centrosymmetric [Ag(othf)]<sub>2</sub> units and have the same Ag–Ag distance of 2.823(1) Å [Ag–O 2.188(9), 2.220(9), 2.257(8), 2.205(9) Å; O–Ag–O 163.8(3), 154.5(3)° for **4**; and Ag–O 2.179(6), 2.220(6), 2.244(6), 2.205(6) Å; O–Ag–O 163.9(2), 155.1(2)° for **5**]. However, the mode of self-assembly in **4** and **5** is different from that in **1** and **3**, being accomplished with a connection of one ring carbonyl oxygen and one of the carboxylato oxygens to different silver(I) atoms, respectively. Also, the polymer sheet **2** can be compared with a stair-like polymer {[Ag<sub>2</sub>(*R*-othf)(*S*-othf)]<sub>n</sub> **6**

**Table 2** Antimicrobial activities of **1–3** evaluated by the minimum inhibitory concentration (MIC: µg mL<sup>−1</sup>)

Microbe	<b>1</b>	<b>2</b>	<b>3</b> <sup>a</sup>
<i>Escherichia coli</i>	15.7	15.7	7.9
<i>Bacillus subtilis</i>	31.3	31.3	31.3
<i>Staphylococcus aureus</i>	31.3	31.3	15.7
<i>Pseudomonas aeruginosa</i>	15.7	15.7	7.9
<i>Candida albicans</i>	7.9	7.9	7.9
<i>Saccharomyces cerevisiae</i>	15.7	15.7	7.9
<i>Aspergillus niger</i>	15.7	15.7	500
<i>Penicillium citrinum</i>	15.7	15.7	250
<i>Aspergillus terreus</i>			1000
<i>Rhizopus stolonifer</i>			15.7
<i>Chaetomium globosum</i>			7.9
<i>Cladosporium cladosporioides</i>			7.9
<i>Penicillium islandicum</i>			15.7
<i>Aureobasidium pullulans</i>			7.9
<i>Fusarium moniliforme</i>			31.3

<sup>a</sup> Ref. 10(b).

of centrosymmetric dimers with an Ag–Ag separation of 2.781(1) Å [Ag–O 2.178(3), 2.250(3) Å; O–Ag–O 164.8(1)°].<sup>10c</sup> Complexes **4–6** also showed a wide ranging effective antimicrobial activity.<sup>10c</sup>

As to the fundamental units of **1–3**, the centrosymmetric dimers formed by two carboxylates and two silver(I) ions have been observed in silver(I)–amino acid complexes such as [Ag<sub>2</sub>(β-ala)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> [Ag–Ag 2.855(4) Å, O–Ag–O 161.6(8)°]<sup>12a,b</sup> and [Ag<sub>2</sub>(Hglygly)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> [Ag–Ag 2.92 Å, O–Ag–O 160°],<sup>12c</sup> and also in several silver(I) complexes such as [Ag<sub>2</sub>(Et<sub>3</sub>Bet)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> [Et<sub>3</sub>Bet = Et<sub>3</sub>N<sup>+</sup>CH<sub>2</sub>CO<sub>2</sub><sup>−</sup>, Ag–Ag 2.928(1) Å, O–Ag–O 160.9(1)°],<sup>12d</sup> {[Ag<sub>2</sub>(Et<sub>3</sub>Bet)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>]<sub>n</sub> [Ag–Ag 2.856(2) Å, O–Ag–O 163.6(1)°]<sup>12d</sup> and [Ag<sub>2</sub>(C<sub>9</sub>H<sub>8</sub>NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2H<sub>2</sub>O [C<sub>9</sub>H<sub>8</sub>NO<sub>3</sub> = *N*-acetylanthranilate, Ag–Ag 2.831(2) Å, O–Ag–O 160.91(1)°].<sup>12e</sup>

### Antimicrobial activities

Antimicrobial activities of the silver(I) complexes **1** and **2**, together with the results of **3** as a comparison, and of the “free” ligands are listed in Table 2, as estimated by minimum inhibitory concentrations (MIC; µg mL<sup>−1</sup>).

Antimicrobial activities of the “free” ligands, *R*- and *S*-H<sub>2</sub>pyrrld, in terms of the minimum inhibitory concentration (MIC; µg mL<sup>−1</sup>) were estimated as >1000 µg mL<sup>−1</sup> for bacteria, yeast and mold, and thus showed no activity. As previously shown,<sup>10a,d</sup> the Ag<sup>+</sup> ion, as aqueous AgNO<sub>3</sub>, 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** and **2** showed a wide range of remarkable and effective activities against Gram-negative and -positive (*B. subtilis* and *S. aureus*) bacteria and yeast (*C. albicans* and *S. cerevisiae*), and even against two tested molds (*A. niger* and *P. citrinum*) (Table 2). In comparing the antimicrobial activities of **1–3**, an anomalous behavior was observed only in **3**; it shows an unusual effect against some molds (*A. niger*, *P. citrinum* and *A. terreus*). However, this is likely to be an artifact, because such an unusual effect has not been found within the closely related silver(I) complexes **4–6**.<sup>10c</sup> Moreover, the silver(I) complexes with D-, L- and DL-aspartic acid ligands have shown identical antimicrobial activities.<sup>10f</sup> Thus, it should be considered that the anomalous action of **3** arises from some experimental factors and, therefore, the antimicrobial actions of **1–3** are similar. These results indicate that the coordination donor atom to the silver(I) center, namely, the weaker silver(I)–oxygen bonding, plays a key role in the antimicrobial activities, with replacement by biological ligands being possible.<sup>10</sup> These facts are also

consistent with the results of the three water-soluble Ag–O bonding complexes **4–6**.<sup>10c</sup>

## Conclusion

Two water-soluble silver(I) complexes showing wide ranging remarkable and effective antimicrobial activity {[Ag(*R*-Hpyrrld)]<sub>2</sub>}, **1** and {[Ag<sub>2</sub>(*R*-Hpyrrld)(*S*-Hpyrrld)]<sub>n</sub>} **2** have been prepared and their crystal structures determined by X-ray crystallography. The enantiomeric complexes, **1** and **3**, in the solid state were right- and left-handed chiral helical polymers, respectively, while the racemic complex **2** was a polymer sheet, all formed by self-assembly of Ag<sub>2</sub>(carboxylato-*O,O'*)<sub>2</sub> units. The mode of self-assembly of the dimeric units has been compared in **1–3** and, also, in the related complexes **4–6**. The antimicrobial activities observed in **1–3** evidence that the silver(I)–oxygen bonding properties, rather than the chiral helical or achiral polymer structures in the solid state, play a significant role. Complexes **1–3** are also of interest as a possible new type of solid-state inorganic polymer.

## Experimental

### Materials

The following were reagent grade and used as received: (*R*)-(+)- and (*S*)-(–)-2-pyrrolidone-5-carboxylic acid (*R*- and *S*-H<sub>2</sub>pyrrld, respectively) (Aldrich), Ag<sub>2</sub>O, DMSO, acetone (Wako); D<sub>2</sub>O (99.9 D atom %) (Isotec).

### 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<sup>–1</sup> between 30 and 500 °C. Infrared spectra were recorded on a Jasco FT-IR 300 spectrometer in KBr discs at room temperature.

<sup>1</sup>H NMR (399.65 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (100.40 MHz) spectra 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. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the complexes were measured in D<sub>2</sub>O solution with reference to internal DSS. Chemical shifts are reported on the δ scale and resonances downfield of DSS (δ 0) are recorded as positive.

Solid-state <sup>13</sup>C NMR (75.58 MHz) spectra were measured using a JEOL JNM-ECP 300 FT-NMR spectrometer equipped with a cross-polarization (CP)/magic angle spinning (MAS) accessory. The <sup>13</sup>C NMR chemical shifts were calibrated indirectly through external hexamethylbenzene [17.3 ppm relative to TMS (δ 0)]. The experimental errors of the isotropic <sup>13</sup>C NMR chemical shift values were estimated to be about 0.5 ppm.

### Synthesis

{[Ag(*R*-Hpyrrld)]<sub>2</sub>}, **1**. To a suspension of 0.232 g (1.0 mmol) of Ag<sub>2</sub>O in 10 mL water was added a solution of 0.260 g (2.0 mmol) of *R*-H<sub>2</sub>pyrrld in 10 mL water. During 2 h stirring, the black suspension gradually changed to a clear orange solution. Unreacted black powder of Ag<sub>2</sub>O was filtered off through a membrane filter (JV 0.1 μm). Vapor diffusion of the clear colorless filtrate with external acetone gave colorless needle crystals, which were collected on a membrane filter (JG 0.2 μm), washed with diethyl ether (100 mL × 2) and dried *in vacuo*. Colorless needle crystals of **1** obtained in 0.27 g (57.4%) yield were soluble in water, sparingly soluble in DMSO, but insoluble in most organic solvents {Found: C, 25.63; H,

2.22; N, 5.89. Calc. for C<sub>5</sub>H<sub>6</sub>NO<sub>3</sub>Ag or [Ag(*R*-Hpyrrld)] as a monomer unit: C, 25.45; H, 2.56; N, 5.94%}. TG/DTA data: no weight loss was observed prior to decomposition. Decomposition began around 182 °C with an exothermic peak at 204 °C. Prominent IR bands in the 1700–400 cm<sup>–1</sup> region (KBr disc): 1676vs, 1594vs, 1408s, 1299s, 1154w, 1106w, 1043w, 721m, 497w cm<sup>–1</sup>. <sup>1</sup>H NMR (D<sub>2</sub>O, 25.2 °C): δ 1.98–2.07 (H4a, m, 1H), 2.37–2.41 (H3, t, 2H), 2.45–2.55 (H4b, m, 1H), 4.16–4.20 (H5, dd, 1H). <sup>13</sup>C NMR (D<sub>2</sub>O, 25.9 °C): δ 28.1 (C4), 32.4 (C3), 61.0 (C5), 183.0 (C6), 184.5 (C2). Solid-state <sup>13</sup>C NMR (23.8 °C): δ 26.3, 28.3 (C4); 30.2, 33.0 (C3); 59.2 (C5); 177.9, 180.2 (C6); 182.2 (C2).

{[Ag<sub>2</sub>(*R*-Hpyrrld)(*S*-Hpyrrld)]<sub>n</sub>} **2**. Compound **2** was isolated as a powder by similar work-up to **1** using a 1:1 mixture of *R*- and *S*-Hpyrrld. The milk-white powder obtained in 0.41 g (86.2%) yield was soluble in water, sparingly soluble in DMSO, but insoluble in most organic solvents. Single crystals of **2** were grown by vapor diffusion of an aqueous solution of **2** with external acetone (Found: C, 25.65; H, 2.20; N, 6.02%). TG/DTA data: no weight loss was observed prior to decomposition. Decomposition began around 170 °C with an exothermic peak at 188 °C. Prominent IR bands in the 1700–400 cm<sup>–1</sup> region (KBr disc): 1676vs, 1593vs, 1408s, 1299s, 1154w, 1106w, 1043w, 1010w, 721m, 497m cm<sup>–1</sup>. <sup>1</sup>H NMR (D<sub>2</sub>O, 20.4 °C): δ 2.00–2.08 (H4a, m, 1H), 2.38–2.43 (H3, t, 2H), 2.47–2.56 (H4b, m, 1H), 4.16–4.20 (H5, dd, 1H). <sup>13</sup>C NMR (D<sub>2</sub>O, 20.4 °C): δ 28.2 (C4), 32.5 (C3), 61.1 (C5), 182.8 (C6), 184.3 (C2). Solid-state <sup>13</sup>C NMR (23.9 °C): δ 29.1 (C4), 30.2 (C3), 58.0 (C5), 179.8 (C6), 182.9 (C2).

### X-Ray crystallography

The intensity data for **1** were collected at 296 K on a Rigaku R-Axis RAPID imaging-plate diffractometer and those for **2** were collected at 296 K on a Rigaku AFC5S diffractometer. The structures were solved by direct methods followed by subsequent difference Fourier calculation and refined by a full-matrix least-squares procedure using the TEXSAN package.<sup>13</sup>

**Crystal data for 1.** C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>Ag<sub>2</sub>, *M* = 471.95, monoclinic, space group *P*2<sub>1</sub> (no. 4), *a* = 5.196(1), *b* = 12.740(3), *c* = 9.716(2) Å, β = 94.820(3)°, *V* = 640.9(1) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 2.446 g cm<sup>–3</sup>, μ = 30.74 cm<sup>–1</sup>, λ(Mo-Kα) = 0.71069 Å, *F*(000) = 456.0. Refinement on 1192 data with *I* ≥ 2.0σ(*I*) gave *R* = 0.050, *R*<sub>w</sub> = 0.069 and GOF = 1.22.

**Crystal data for 2.** C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>Ag<sub>2</sub>, *M* = 471.95, monoclinic, space group *P*2<sub>1</sub>/*n* (no. 14), *a* = 7.459(1), *b* = 5.312(5), *c* = 15.961(1) Å, β = 92.11(1)°, *V* = 631.9(4) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 2.480 g cm<sup>–3</sup>, μ = 31.17 cm<sup>–1</sup>, λ(Mo-Kα) = 0.71069 Å, *F*(000) = 456.0. Refinement on 875 data with *I* ≥ 2.0σ(*I*) gave *R* = 0.034, *R*<sub>w</sub> = 0.025 and GOF = 1.23.

CCDC reference number 186/2198.

See <http://www.rsc.org/suppdata/dt/b0/b006552h/> for crystallographic files in .cif format.

### Antimicrobial activity

Antimicrobial activities of silver(I) complexes were estimated by the minimum inhibitory concentration (MIC: μg mL<sup>–1</sup>) as described elsewhere.<sup>10b,c</sup>

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