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FULL PAPER

Synthesis and crystal structure of a hexanuclear silver(I) cluster $[Ag(Hmna)]_6\cdot 4H_2O$ (H_2mna = 2-mercaptonicotinic acid) and a supramolecular gold(I) complex $H[Au(Hmna)_2]$ in the solid state, and their antimicrobial activities

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2-Mercaptonicotinic acid (H_2mna = 2-$HS(C_5H_3N)CO_2H$) gave two types of silver(I) complexes by a reaction with Ag_2O suspended in aqueous media; one was a water-insoluble, DMSO-soluble yellow powder $[Ag(Hmna)]_6\cdot 4H_2O$ **1** formed under acidic conditions, and the other was a water-soluble, yellow powder $\{Na[Ag(mna)]\cdot H_2O\}_n$ **2** formed under alkaline conditions. These two complexes were interconverted on changing the acidity of the solution. Crystallization by vapor diffusion of the DMSO and aqueous solutions with external acetone gave pale yellow cubic crystals for **1** and pale yellow plate crystals for **2**, but structure determination was successful only for **1**. The molecular structure of **1** consists of a discrete, hexanuclear silver(I) cluster with the two silver(I) triangles linked by the mercaptonicotinate anions, the geometry around each silver(I) atom being constructed by one aromatic nitrogen atom and two μ-S atoms and the two weak silver(I)–silver(I) interactions. The corresponding gold(I) complex as a water-insoluble, DMSO-soluble yellow powder, $H[Au(Hmna)_2]$ **3**, was prepared by treatment with aqueous HCl of $Na_3[Au(mna)_2]\cdot 2H_2O$ **4** which was obtained by a 1 : 4 : 8 molar ratio reaction of $Na[AuCl_4]\cdot 2H_2O$: H_2mna : NaOH in aqueous solution. Complex **3** crystallized as yellow needle crystals by vapor diffusion of the DMSO solution with external acetone. Its crystal structure with a monomeric 2-co-ordinate AuS_2 core shows a supramolecular arrangement by a π–π stacking interaction between two pyridine rings (face-to-face separation 3.42(2)–3.52(1) Å) and, also, by two different hydrogen-bonding interactions; one formed between the carboxyl proton and aromatic nitrogen, and the other an unusual single-mode hydrogen bond between two twisted carboxyl groups. The complexes were also characterized by elemental analysis, TG/DTA, FT-IR, ^{1}H and ^{13}C NMR for **1**–**4**, as well as ^{109}Ag NMR for **2**. Noteworthy antimicrobial activities for **1**–**4**, evaluated by minimum inhibitory concentration, were observed.

There is currently considerable interest in the co-ordination chemistry of coinage metals such as silver(I) and gold(I) with biological and/or medicinal activities.[1–6] The studies of silver(I) complexes have mostly been focused so far on their antiethylene[2a,b] and antimicrobial activities,[2c,d] those of gold(I) complexes mostly on their antiarthritic,[1,3] antitumor,[1,4] and, recently, antimicrobial activities.[5,6l–n] The molecular design and structure determination of such silver(I) and gold(I) complexes are an intriguing aspect of bioinorganic chemistry, inorganic syntheses and metal-based drugs. In the medicinally or pharmaceutically active compounds of silver(I) and gold(I), most complexes formed with thiol and nitrogen-containing heterocyclic ligands are harder to crystallize and are believed to be polymeric.[1e,3g,6a–c]

We have been interested in the molecular design and structure determination of biologically active silver(I) and gold(I) complexes with common ligands.[6] We have realized a set of sodium metal(I) thiomalates, *e.g.* $\{Na[Ag(Htma)]\cdot 0.5H_2O\}_n$ (n = 24–34; H_3tma = thiomalic acid)[6a,b] and $\{Na_2[Au(tma)]\cdot 1.75H_2O\}_n$ (n = 3–10),[6e] and a set of metal(I) 2-mercaptobenzoates, *e.g.* $[Ag(Hmba)]_n$ (H_2mba = 2-mercaptobenzoic acid),[6c] $\{Na[Ag(mba)]\cdot H_2O\}_n$ (n = 21–27),[6c] and $Na_3[Au(mba)_2]\cdot 5H_2O$.[6d] The oligomeric silver(I) complexes have displayed effective antimicrobial activities against selected bacteria, yeast and mold,[6a,c] whereas the gold(I) complexes have shown effective antiarthritic activities.[6f] However, most of the compounds were difficult to crystallize.

In relation to $\{Na_2[Au(tma)]\}_n$, commercial $\{Na_{2-x}H_x[Au(tma)]\}_n$ as an antiarthritic drug (myochrisine), believed to be most difficult to crystallize, has recently been crystallized by hanging-drop vapor diffusion and the crystal structure of $\{Na_2Cs[Au_2(Htma)(tma)]\}_n$ determined.[3g] With respect to $Na_3[Au(mba)_2]$, we have very recently been successful in determining the crystal structure of $\{K_3[Au(mba)_2]\}_2$, which is a dimer in the solid state through an Au–Au interaction, *i.e.* an aurophilic interaction.[6g] On the other hand, since our first report in 1995,[6c] considerable efforts have been made to get crystals of the water-soluble silver(I) 2-mercaptobenzoate, $\{Na[Ag(mba)]\}_n$, prepared from a reaction with molar ratio $AgNO_3$: H_2mba : NaOH = 1 : 1 : 2. Very recently, the salts $M_{12}[Ag_8(mba)_{10}]\cdot nH_2O\cdot m$MeOH (M = K, n = 12, m = 0; M = Na, n = 5, m = 2), obtained from the molar ratio Ag_2O : H_2mba : MOH = 1 : 4 : 8 in aqueous solution, have been crystallized and their crystal structures determined.[6h] However, the Ag_8 clusters are precursors of the original $\{M[Ag(mba)]\}_n$ (M = Na or K) complexes, crystallization of which is still difficult.

For the molecular design of new coinage metal(I) complexes we used here a polyfunctional ligand, *i.e.* 2-mercaptonicotinic acid (H_2mna = 2-$HS(C_5H_3N)CO_2H$), with pyridine N, thiol S and carboxylic O donor atoms, and obtained two silver(I) complexes, $[Ag(Hmna)]_6\cdot 4H_2O$ **1** and $\{Na[Ag(mna)]\cdot H_2O\}_n$ **2**, and two gold(I) complexes, $H[Au(Hmna)_2]$ **3** and $Na_3[Au(mna)_2]\cdot 2H_2O$ **4**. Complex **1** has been used as a precursor for the preparation of $[Ag(Hmna)(PPh_3)_n]$ (n = 2 or 3).[6i] X-Ray crystallography of **1** and **3** revealed unexpected structures in the solid state; the molecular structure of **1** was a novel hexanuclear silver(I) cluster and, on the other hand, that of **3** was a 2-co-ordinate AuS_2 complex in a supramolecular arrangement of a

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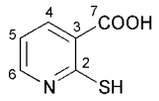

H_2mna

three-dimensional network formed by a π–π stacking interaction between two pyridine rings and, also, by two different hydrogen-bonding interactions. Herein, we report the full details of the synthesis of **1**–**4** and the X-ray crystallography of **1** and **3**. Also reported are noteworthy antimicrobial activities for **1**–**4** evaluated with minimum inhibitory concentration.

Results and discussion

Synthesis and compositional characterization of complexes 1–4

The composition and molecular formula of the two silver(I) complexes **1** and **2** and the two gold(I) complexes **3** and **4** were consistent with elemental analyses, TG/DTA, FT-IR, solution ^{1}H and ^{13}C NMR as shown in the Experimental section, and those of **1** and **3** were also supported by single-crystal X-ray structure analyses. The presence of solvated water molecules in **1**, **2** and **4** was confirmed by weight losses observed in TG/DTA measurements. The syntheses of **2** and **1** are represented in eqn. (1) and (2), respectively, and those of **4** and **3** in (3) and (4), respectively, where $Na_2(mna)_2$ is a disulfide (RS–SR) form

$$Ag_2O + 2\ H_2mna + 2\ NaOH \longrightarrow \underset{\mathbf{2}}{(2/n)\{Na[Ag(mna)]\}_n} + 3\ H_2O \quad (1)$$

$$\underset{\mathbf{2}}{(6/n)\{Na[Ag(mna)]\}_n} + 3\ H_2SO_4 \longrightarrow \underset{\mathbf{1}}{[Ag(Hmna)]_6} + 3\ Na_2SO_4 \quad (2)$$

$$Na[AuCl_4]\cdot 2H_2O + 4\ H_2mna + 8\ NaOH \longrightarrow \underset{\mathbf{4}}{Na_3[Au(mna)_2]} + 10\ H_2O + Na_2(mna)_2 + 4\ NaCl \quad (3)$$

$$\underset{\mathbf{4}}{Na_3[Au(mna)_2]} + 3\ HCl \longrightarrow \underset{\mathbf{3}}{H[Au(Hmna)_2]} + 3\ NaCl \quad (4)$$

of mna^{2-}. The two free acid forms **1** and **3** can be changed to sodium salts **2** and **4**, respectively, by treatment with aqueous NaOH solution.

The solid FT-IR spectra of complexes **1**–**4** show the disappearance of the S–H stretching band around 2560 cm^{-1} due to the "free" ligand, suggesting M–S bond formation. A very intense band around 3400 cm^{-1} observed for **1**, **2** and **4** is attributed to the presence of hydrated water in these compounds. Multiple weak bands observed in the 3000–2500 cm^{-1} region of **1** and **3** are also attributed to the presence of a protonated carboxyl group. In **1**–**4** the mna^{2-} ligand co-ordinating to the metal(I) center was observed as three ^{1}H NMR and six ^{13}C NMR signals.

^{109}Ag NMR spectra in D_2O measured at room temperature exhibited only one sharp signal at δ 1029 for complex **2**, suggesting that all silver(I) ions in this oligomeric complex are equivalent. This resonance is compared with those of the related oligomeric silver(I) complexes co-ordinated only by bridging sulfur atoms, measured at room temperature in D_2O: δ 855.6 for $\{Na[Ag(mba)]\}_n$,[6c] δ 868.7 for $\{Na[Ag(Htma)]\}_n$,[6a] and δ 508.7 and 927.8 as sharp and broad signals, respectively, for $K_{12}[Ag_8(mba)_{10}]$.[6h]

Crystal and molecular structures of complexes 1 and 3

The molecular structures of complexes **1** and **3** with the atom numbering scheme are depicted in Fig. 1 and 2, respectively.

Table 1 Selected bond distances (Å) and bond angles (°) for complexes **1** and **3**

1			
Ag1···Ag2	2.911(1)	Ag2–S3	2.497(3)
Ag1···Ag3^i	2.924(1)	Ag3–S2^i	2.459(2)
Ag2···Ag3^i	3.1129(8)	Ag3–S1	2.505(2)
Ag1–S3^i	2.490(2)	Ag1–N1a	2.273(5)
Ag1–S1	2.490(2)	Ag2–N1	2.317(5)
Ag2–S2	2.465(2)	Ag3–N1b	2.294(5)
Ag1–Ag2–Ag3^i	57.97(3)	Ag3^i–Ag1–S1	129.14(4)
Ag1–Ag3^i–Ag2	57.54(2)	Ag3^i–Ag2–S2	50.71(4)
Ag2–Ag1–Ag3^i	64.48(3)	Ag3^i–Ag2–S3	102.21(4)
Ag1–Ag2–S2	76.50(4)	Ag1–Ag2–N1	88.6(1)
Ag1–Ag2–S3	135.70(4)	Ag1–Ag3^i–N1b^i	91.3(1)
Ag1–Ag3^i–S2	76.32(4)	Ag2–Ag1–N1a	87.6(1)
Ag1–Ag3^i–S1^i	133.99(4)	Ag2–Ag3^i–N1b^i	148.7(1)
Ag2–Ag1–S3^i	128.05(4)	Ag3^i–Ag1–N1a	87.6(1)
Ag2–Ag1–S1	76.49(4)	Ag3^i–Ag2–N1	146.5(1)
Ag2–Ag3^i–S2	50.88(4)	Ag1–S3^i–Ag2^i	92.02(5)
Ag2–Ag3^i–S1^i	99.17(4)	Ag1–S1–Ag3	93.70(5)
Ag3^i–Ag1–S3^i	75.54(4)	Ag2–S2–Ag3^i	78.41(5)
3			
Au1–S1	2.283(3)	O2···N1	2.77(1)
O1···O1^{ii}	2.46(2)		
S1–Au1–S1^i	179.3(2)	Au1–S1–C2	107.0(3)

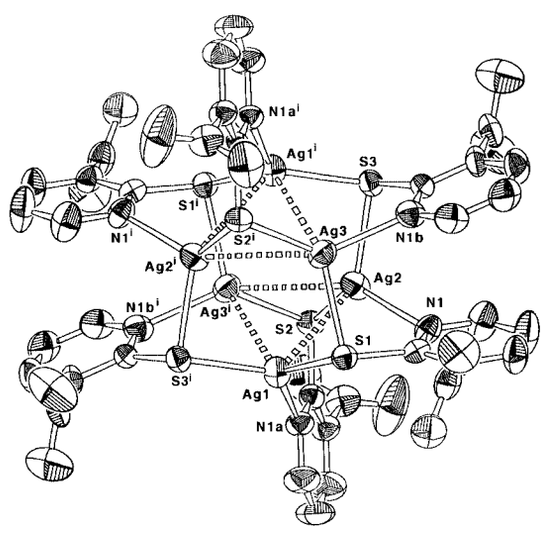

Fig. 1 Molecular structure of $[Ag(Hmna)]_6$ **1** with 50% probability thermal ellipsoids (symmetry operation i: $-x + 2$, $-y$, $-z$).

Selected bond distances and angles with their estimated standard deviations are listed in Table 1.

The carboxyl groups of complex **1** participate neither in the co-ordination to the silver(I) center nor in the intermolecular interactions through hydrogen bonds. Therefore, this silver(I) complex is a discrete monomer in the solid state. The molecular structure consists of neutral hexanuclear $[Ag(Hmna)]_6$, which is composed of two distorted silver triangles (Ag···Ag 2.911(1), 2.924(1) and 3.1129(8) Å. Ag–Ag–Ag: 57.97(3), 57.54(2) and 64.48(3)°) as the building-block unit (Fig. 1). The Ag···Ag separations are intermediate between that in metallic silver (2.88 Å)[7a] and twice the van der Waals radius for silver (3.44 Å),[7b,c] indicating the existence of weak metal–metal interactions.[8] In **1** the two silver triangle units are linked by four μ-S atoms of the $Hmna^-$ ligands. The two silver atoms (Ag2^i and Ag3) within the triangle are bridged by one μ-S atom (S2^i). Thus, there are two kinds of co-ordination modes of the sulfur atoms, *i.e.* two intra-triangle μ-bonding modes and four inter-triangle μ-bonding modes. The co-ordination environment around each silver atom is constructed by the two weak silver(I)–silver(I) interactions, two μ-S atoms and one mono-

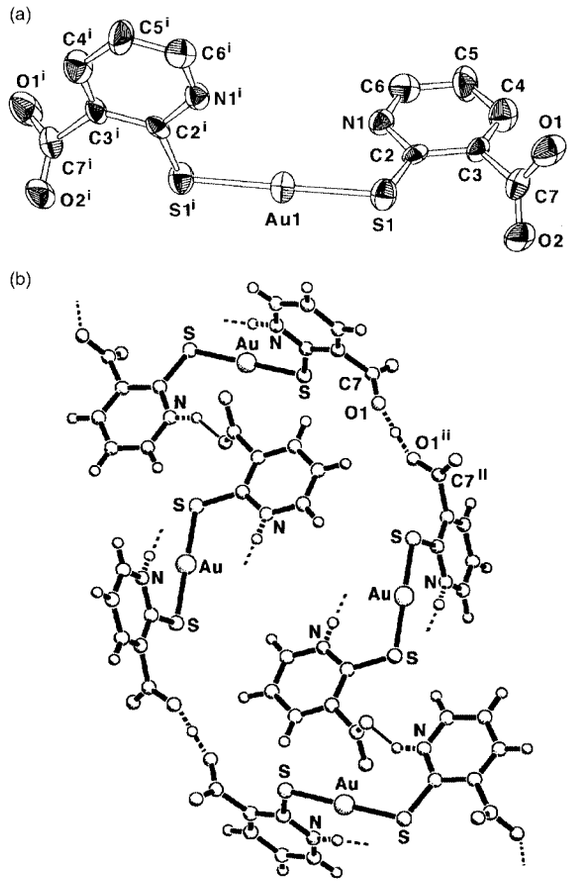

Fig. 2 (a) Molecular structure of H[Au(Hmna)$_2$] **3** with 50% probability thermal ellipsoids (symmetry operation i: $x-y$, $-y$, $\frac{1}{2}+z$) and (b) its intermolecular association through two different hydrogen-bonding interactions and π–π stacking interaction between two pyridine rings (symmetry operation ii: $\frac{2}{3}+y$, $-\frac{2}{3}+x$, $\frac{5}{6}-z$).

dentate nitrogen atom of the Hmna$^-$ ligands. This Ag_6 cluster structure can be compared with that of the recently found Ag_8 cluster $K_{12}[Ag_8(mba)_{10}]\cdot 12H_2O$[6h] which has a discrete, centrosymmetric octanuclear unit consisting of two butterfly-type Ag_4S_4 subunits bridged by two μ_3-S atoms. In the Ag_8 cluster none of the carboxyl groups participates in co-ordination to the silver(I) centers, and the Ag···Ag separations in the Ag_4S_4 cores range from 2.875(4) to 3.155(4) Å. The hexanuclear structure with a center of inversion in **1** is also quite different from those of $[\{Ag(SR)\}_6]$[9b,g] (HSR = 3-(*tert*-butyldimethylsilyl)pyridine-2-thione) and $[Cu_6(SC_5H_4N)_6]$[9h] with distorted octahedral M_6 cores and also from that of $[Ag_6(\mu_3\text{-}SC_5H_4N)_4(\mu_4\text{-}SC_5H_4N)_2]_n$ with a one-dimensional chain structure (SC_5H_4N = pyridine-2-thionate).[9a]

The molecular structure of complex **3** (Fig. 2(a)) has a 2-co-ordinate linear geometry with an AuS_2 core (Au–S 2.283(3) Å, S–Au–S 179.3(2)°). There are no inter- or intra-molecular gold(I)–gold(I) interactions. This structure is comparable with those of monomeric 2-co-ordinate AuS_2 core complexes such as $Na_3[Au(S_2O_3)_2]\cdot 2H_2O$ (Au–S 2.28(1) Å, S–Au–S 176.5°),[10a] $[NH_4]_5[Au((\pm)\text{-tma-}S)_2]\cdot H_2O$ (Au–S 2.277(6), 2.251(6) Å, S–Au–S 178.8(2)°),[10b] $[NH_4]_5[Au(R\text{-tma-}S)_2]\cdot H_2O$ (Au–S 2.284(4), 2.266(4) Å, S–Au–S 176.03(12)°),[10b] $[N(PPh_3)_2][Au(SR)_2]$ (HSR = benzoxazole-2(1*H*)-thione; Au–S 2.281(2), 2.283(2) Å, S–Au–S 175.11(5)°),[10c] $[NEt_4][Au(SAd)_2]$ (AdS^- = adamantane thiolate anion; Au–S 2.298(4) Å, S–Au–S 180.0°),[10d] and the dimeric complex $\{K_3[Au(mba)_2]\}_2$ through a gold(I)-gold(I) interaction (Au···Au 3.1555(7) Å, Au–S 2.288(3), 2.277(3), 2.276(3), 2.285(3) Å, S–Au–S 174.5(1), 177.1(1)°).[6g]

The crystal structure of complex **3** consists of a supramolecular three-dimensional network as shown in Fig. 2(b), which comprises a π–π stacking interaction between two pyridine rings (3.42(2)–3.52(1) Å), and two different types of hydrogen-bonding interactions; one formed between the carboxyl proton and the pyridine nitrogen atom (O···N 2.77(1) Å) and the other an unusual single-mode hydrogen bond formed between the two twisted carboxyl groups (O···O 2.46(2) Å). The latter interaction comes from the non-coplanarity of two carboxyl groups (torsion angle C7–O1–O1^{ii}–C7^{ii} 140(2)°). Examples of hydrogen-bonding interactions of a carboxyl proton with heteroatoms such as S and N have been reported, but only a few. Such examples have been recently found in [Au(Hmna)-(PPh_3)],[6i] which consists of repeated hydrogen bonds between the protonated carboxyl group and the pyridine nitrogen atom (O···N 2.66 Å) and lacks of hydrogen bonds between the carboxyl groups. Also, hydrogen bonding interactions are observed between the carboxyl proton and the thiolate sulfur atom in the complex [Au(3-Hmba)(PPh_3)] (3-H_2mba = 3-mercaptobenzoic acid) with gold(I)–gold(I) interaction (Au···Au 3.0854(3) Å, O···S 3.154(4) Å, O–H···S angle 175°).[6j] In relation to **3**, the supramolecular structure of [Au-(Hmba)(RNC)] (R = *t*-Bu or mesityl), which is governed by Au···Au interactions (3.157(2) and 3.3186(5) Å, respectively) and hydrogen bonding through the carboxylic acid groups, is noteworthy.[10e]

The crystal structure determination of complex **2** has been attempted several times using different crystals, but there remained a problem due to disorder of the carboxyl groups revealed by a large thermal parameter.

Antimicrobial activities of complexes 1–4

Antimicrobial activities of the two silver(I)–mercaptonicotinate complexes **1** and **2**, and the corresponding gold(I) complexes **3** and **4**, together with those of free H_2mna are listed in Table 2, as estimated by the minimum inhibitory concentration (MIC; $\mu g\ mL^{-1}$).

Antimicrobial activities of the "free" ligand were estimated as >1000 $\mu g\ mL^{-1}$ for four bacteria (*E. coli*, *B. subtilis*, *S. aureus* and *P. aeruginosa*), two yeasts (*C. albicans* and *S. cerevisiae*) and two molds (*A. niger* and *P. citrinum*), showing a lack of activity against all test organisms. Complex **1** showed a wide spectrum of effective activities against four bacteria, one yeast (*C. albicans*) and six molds. On the other hand, **2** showed effective activities against two Gram-negative bacteria (*E. coli* and *P. aeruginosa*) and four molds (*R. stolonifer*, *A. pullulans*, *F. moniliforme* and *C. sphaerospermum*), but no activity against two Gram-positive bacteria (*B. subtilis* and *S. aureus*), two yeasts and two molds. These antimicrobial activities are different from those of the previous Ag–S bonded complexes $[Ag(Hmba)]_n$ and $\{Na[Ag(mba)]\cdot H_2O\}_n$, which have shown effective activities against the four bacteria and one yeast (*S. cerevisiae*), but no activity against the six molds.[6c]

The spectra of antimicrobial activities observed in the Ag–S bonded compounds have so far been narrower than those in the silver(I)-N bonded compounds such as $[Ag(im)]_n$ (Him = imidazole), $[Ag(1,2,4\text{-triz})]_n$ (Htriz = triazole), and $[Ag(tetz)]_n$ (Htetz = tetrazole).[6k,l] Recently, we have proposed that one key factor determining the spectra of antimicrobial activities is the kind of atom co-ordinated to the silver(I) atom, *i.e.* the ease of ligand replacement, rather than the solid-state structure and the solubility.[6k] The Ag–N bonding with ease of ligand replacement results in wider spectra of antimicrobial activities. Since **1** and **2** contain extra Ag–N bonds compared with $[Ag(Hmba)]_n$ and $\{Na[Ag(mba)]\cdot H_2O\}_n$, their antimicrobial activities, different from those of $[Ag(Hmba)]_n$ and $\{Na[Ag(mba)]\cdot H_2O\}_n$, should be interpreted by taking into account this bonding factor.

On the other hand, the gold(I) complexes tested here showed antimicrobial activities only against bacteria; **3** showed effective activities against two Gram-negative bacteria and moderate activities against two Gram-positive bacteria, while **4** showed

Table 2 Antimicrobial activities of silver(I) and gold(I) complexes **1**–**4** evaluated by minimum inhibitory concentration (MIC; μg mL^{-1})

Microbe	H_2mna	$[Ag(Hmna)]_6$ **1**	$\{Na[Ag(mna)]\}_n$ **2**	$H[Au(Hmna)_2]$ **3**	$Na_3[Au(mna)_2]$ **4**
Escherichia coli	>1000	25	15.7	7.9	62.5
Bacillus subtilis	>1000	25	>1000	62.5	250
Staphylococcus aureus	>1000	25	>1000	125	>1000
Pseudomonas aeruginosa	>1000	12.5	31.3	62.5	>1000
Candida albicans	>1000	50	>1000	>1000	>1000
Saccharomyces cerevisiae	>1000		>1000	>1000	>1000
Aspergillus niger	>1000	100	>1000	>1000	>1000
Penicillium citrinum	>1000	50	>1000	>1000	>1000
Rhizopus stolonifer		25	25		
Aureobasidium pullulans		100	100		
Fusarium moniliforme		50	50		
Cladosporium sphaerospermum		12.5	12.5		

moderate activities against one Gram-negative bacterium (*E. coli*) and modest activities against one Gram-positive bacterium (*B. subtilis*). The antimicrobial activities of **4** were similar to those of $Na_3[Au(mba)_2]\cdot 5H_2O$. These results are unusual and have not been observed so far for silver(I) complexes. Recently, we have evidenced that the mode of antimicrobial action of phosphinegold(I) complexes with N- and S-donor ligands is quite different from that of the corresponding silver(I) complexes.[6m,n] Thus, the mode of antimicrobial action of **3** and **4** should be substantially different from that of **1** and **2**.

Conclusion

The 2-mercaptonicotinic acid (H_2mna) ligand provided silver(I) and gold(I) complexes with unexpected structures in the solid state, *i.e.* a hexanuclear silver(I) cluster **1** and a gold(I) thiolate **3** with a 1:2 type molecular arrangement. These features are in contrast to those of the recent coinage metal(I) complexes with 2-mercaptobenzoic acid (H_2mba) such as $M_{12}[Ag_8(mba)_{10}]$ (M = K or Na),[6d,h] $\{M_3[Au(mba)_2]\}_2$,[6g] and [Au(Hmba)(RNC)] (R = *t*-Bu or mesityl).[10e] These differences result from a substantial difference in the pyridine or benzene ring of the ligands. The coinage metal(I) complexes described here have shown marked antimicrobial activities. However, the mode of action of **3** and **4** can not be interpreted in the same way as that of **1** and **2**.

Experimental

Materials

All chemicals were reagent grade and used as received: 2-mercaptonicotinic acid, Ag_2O, 1.0 M NaOH aqueous solution (quantitative analysis grade), 1.0 M HCl aqueous solution (quantitative analysis grade), 0.5 M H_2SO_4 aqueous solution (quantitative analysis grade), ethanol, acetone, diethyl ether, acetonitrile, DMSO (all from Wako); D_2O, DMSO-d_6, (Isotec).

Instrumentation/analytical procedures

The CHNS analyses were performed using a Perkin-Elmer PE2400 series II CHNS/O Analyzer. Thermogravimetric (TG) and differential thermal analyses (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} for complex **1** and 1 °C min^{-1} for **2**–**4** between 20 and 500 °C. Infrared spectra were recorded on a JASCO FT-IR 300 spectrometer in KBr disks at room temperature, ^{1}H (399.65) and ^{13}C-{^{1}H} NMR (100.40 MHz) spectra in solution at 25 °C 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 and ^{13}C-{^{1}H} NMR spectra of complexes in D_2O solution were measured with reference to an internal standard of DSS (sodium 4,4-dimethyl-4-silapentane-1-sulfonate) and those in DMSO-d_6 solutions with reference to an internal standard of TMS. Chemical shifts are reported on the δ scale and resonances downfield of DSS or TMS (δ 0) are recorded as positive.

^{109}Ag NMR (18.45 MHz) spectra were recorded at 25 °C in 10 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe. Spectra of the complexes were measured in $CDCl_3$ solution with reference to an external standard of saturated $AgNO_3$–D_2O solution by a substitution method. Chemical shifts are recorded as positive for resonances downfield of $AgNO_3$ (δ 0). Spectral parameters for ^{109}Ag NMR include: pulse width 13.2 μs; acquisition time 0.390 s; recycle time 1.39 s; sweep width 21008 Hz.

Synthesis

Water-insoluble complex $[Ag(Hmna)]_6\cdot 4H_2O$ 1. To a stirred suspension of 1.16 g (5.00 mmol) Ag_2O in 20 mL water was added a clear, yellow solution of 1.55 g (10.0 mmol) H_2mna ligand and 20 mL of 1.0 M aqueous NaOH solution (20.0 mmol) dissolved in 40 mL water. The black suspension was stirred for 6 h, followed by passage through a folded filter paper (Whatman No. 5). To the stirred filtrate were added 20 mL of 0.5 M sulfuric acid (10.0 mmol), resulting in the formation of a yellow–green solid. After 1 h stirring the powder was collected on a membrane filter (JG 0.2 μm), washed with 50 mL each of water, acetone and diethyl ether, and dried thoroughly by suction. The yellow–green solid was suspended in 10 mL water, and 10 mL of 1.0 M aqueous NaOH (10.0 mmol) were added. After 1 h stirring the yellow solution was passed through a folded filter paper (Whatman No. 5). To the clear yellow filtrate with stirring were added 10 mL of 0.5 M sulfuric acid (5.00 mmol) and the stirring was continued for 1 h. The yellow solid formed was collected on a membrane filter (JG 0.2 μm), washed with 50 mL each of water, acetone and diethyl ether, and dried thoroughly by suction and then *in vacuo* for 2 h. Yield 1.86 g (67.5%). This procedure was successfully scaled-up by a factor of 2, resulting in a 4.01 g yield (74.0%). The light- and thermally-stable yellow powder obtained was sparingly soluble in DMSO, but insoluble in water and most organic solvents.

Crystallization. An almost saturated DMSO solution (5 mL) containing 0.100 g of the yellow solid was filtered once through a folded filter paper (Whatman No. 5). By vapor diffusion of the filtrate with 20 mL external acetone, pale yellow cubic crystals formed after a few days, which became a yellow powder

out of the solution. Thus, the crystals were sealed in a capillary for X-ray diffraction measurements {Found: C, 26.03; H, 2.01; N, 5.17; S, 11.46. Calc. for $C_{18}H_{16}Ag_3N_3O_8S_3$ or $[Ag(Hmna)]_6 \cdot 4H_2O$: C, 26.30; H, 1.96; N, 5.11; S, 11.70%}. TG/DTA data: weight loss of 3.73% before decomposition (calc. for 4 water molecules of hydration, 4.38%); decomposition began around 200 °C with an endothermic peak at 45 °C and exothermic peaks at 188, 208 and 228 °C. Prominent IR bands in the 1800–400 cm^{-1} region (KBr disc): 1717–1636m, 1577vs, 1560vs, 1490m, 1438m, 1388vs, 1321s, 1250m, 1136m, 1075m, 1047w, 814m, 760m, 734m, 638m and 468m cm^{-1}. ^1H NMR (25 °C, DMSO-d_6): δ 6.75 (1 H, dd, H5, J 5.3), 7.52 (1 H, d, H4, J 7.6) and 7.77 (1 H, d, H6, J 3.7 Hz). ^{13}C NMR (25 °C, DMSO-d_6): δ 118.4 (C5), 132.8 (C3), 135.7 (C4), 150.2 (C6), 161.9 (C2) and 168.5 (C7).

In the synthesis, when $AgNO_3$, instead of Ag_2O, as the starting silver(I) compound was used and/or HNO_3, instead of H_2SO_4, as reprecipitating agent, NO_3^--contaminated compounds were formed and the NO_3^- ion was difficult to remove. When aqueous HCl was used as the reprecipitating agent, light-unstable compounds, contaminated with AgCl and free H_2mna, were obtained.

Water-soluble sodium salt, $\{Na[Ag(mna)]\cdot H_2O\}_n$ 2. To a stirred suspension of 1.17 g (5.00 mmol) Ag_2O in 20 mL water was added a clear, yellow solution prepared by adding 20 mL of 1.0 M aqueous NaOH solution (20.0 mmol) to 1.55 g (10.0 mmol) H_2mna suspended in 10 mL water. The black suspension was stirred overnight, followed by passage through a folded filter paper (Whatman No. 5). The clear yellow–green filtrate was added dropwise to 300 mL ethanol–diethyl ether (1 : 2) resulting in a white oil. The supernatant was discarded by decantation and the white oil washed three times with 150 mL ethanol–diethyl ether (1 : 2). The oil was dissolved in 10 mL water and filtered through a folded filter paper (Whatman No. 2). The clear yellow filtrate was added dropwise to 250 mL ethanol. The yellow–white solid formed was collected on a membrane filter (JG 0.2 μm), washed with ethanol (100 mL × 2), acetone (100 mL × 2) and diethyl ether (100 mL × 2), and dried thoroughly *in vacuo* for 2 h. The hygroscopic, yellow–white powder, which was highly soluble in water, but insoluble in most organic solvents, was obtained in 0.90 g (59.6%) yield. This procedure was also effective for experiments scaled up by a factor of 2, resulting in 2.76 g (91.4%).

Crystallization. The clear yellow solution of the yellow–white solid (1.00 g) dissolved in 5 mL water was filtered through a folded filter paper (Whatman No. 2). By vapor diffusion of the filtrate with external acetone, pale yellow plate crystals formed after a few days which were collected on a membrane filter (JG 0.2 μm), washed with acetone (100 mL × 2) and diethyl ether (100 mL × 2), and dried *in vacuo* for 2 h. Yield 0.90 g (90.0%) {Found (repeat trials for CHN analysis): C, 23.54 (23.81); H, 2.73 (2.11); N, 4.74 (4.73); S, 9.58. Calc. for $C_6H_5AgNNaO_3S$ or $Na[Ag(mna)]\cdot H_2O$ as a monomeric unit: C, 23.86; H, 1.67 ; N, 4.64; S, 10.61%}. TG/DTA data: weight loss of 6.16% below 172 °C (calc. for 1 H_2O 5.97%); decomposition began gradually around 300 °C with an endothermic peak at 62 °C and exothermic peaks at 243, 249, 300 and 329 °C. Prominent IR bands in the 1800–400 cm^{-1} region (KBr disc): 1575vs, 1445m, 1394vs, 1236w, 1224w, 1160m, 1129m, 1082m, 1054w, 853w, 810w, 785w, 735m, 668w, 599w and 471w cm^{-1}. ^1H NMR (25 °C, D_2O): δ 6.73 (1 H, dd, H5, J 5.4), 7.27 (1 H, dd, H4, J 7.3) and 7.82 (1 H, d, H6, J 4.9 Hz). ^{13}C NMR (25 °C, D_2O): δ 121.7 (C5), 136.0 (C3), 141.3 (C4), 151.7 (C6), 161.3 (C2) and 179.3 (C7). ^{109}Ag NMR (25 °C, D_2O): δ 1029 ($\Delta_{1/2}$ 21.8 Hz).

Water-insoluble complex $H[Au(Hmna)_2]$ 3. To 1.00 g (2.51 mmol) of $Na[AuCl_4]\cdot 2H_2O$ dissolved in 10 mL water was added a clear yellow solution prepared by mixing 1.55 g (10.0 mmol) H_2mna suspended in 10 mL water and 20 mL of 1.0 M aqueous NaOH (20.0 mmol), followed by passing through a folded filter paper (Whatman No. 2). The clear yellow filtrate was concentrated to *ca.* 10 mL by a rotary evaporator at 50 °C. The concentrated solution was added dropwise to 300 mL of acetonitrile to give a yellow oil, which was rinsed with (100 mL × 3) acetonitrile. The yellow oil was dissolved in 10 mL water, to which 100 mL of 1.0 M aqueous HCl solution were added. The yellow powder formed was collected on a membrane filter (JG 0.2 μm), washed with water (200 mL × 2), ethanol (200 mL × 2) and then acetone (200 mL × 2), dried thoroughly by suction, and dried *in vacuo* for 2 h. At this stage a DMSO-soluble yellow powder of $H[Au(Hmna)_2]$ was obtained in 1.21 g (95.2%) yield.

Crystallization. 0.27 g (0.53 mmol) of the yellow powder was dissolved in 15 mL DMSO, followed by filtering through a folded filter paper (Whatman No. 2). Vapor diffusion with 30 mL external acetone gave clear yellow needle crystals after 3 days at room temperature, which were collected on a membrane filter (JG 0.2 μm), washed with acetone (100 mL × 2) then ether (100 mL × 2), and dried *in vacuo* for 2 h. During the work-ups the yellow needle crystals changed to a yellow powder. Thus, the single crystal was sealed in a capillary for X-ray diffraction measurement. The relatively light-stable, yellow powder obtained in 0.077 g (28.4%) yield was soluble only in DMSO and insoluble in water and most organic solvents {Found: C, 28.42; H, 1.87; N, 5.40; S, 12.31. Calc. for $C_{12}H_9AuN_2O_4S_2$ or $H[Au(Hmna)_2]$: C, 28.47; H, 1.79; N, 5.53; S, 12.66%}. TG/DTA data: no weight loss before 181 °C; decomposition began gradually around 211 °C with an endothermic peak at 211 °C. Prominent IR bands in the 1800–400 cm^{-1} region (KBr disc): 1658m, 1602s, 1577vs, 1478s, 1434m, 1308m, 1259s, 1207m, 1147m, 1083w, 1042m, 979w, 883w, 799m, 767m, 734m, 717m, 649m, 569w and 470w cm^{-1}. ^1H NMR (25 °C, DMSO-d_6): δ 7.18 (1 H, dd, H5, J 5.5), 8.00 (1 H, s, H4) and 8.30 (1 H, d, H6, J 1.8 Hz). ^{13}C NMR (25 °C, DMSO-d_6): δ 118.1 (C5), 131.6 (C3), 139.5 (C4), 145.7 (C6), 164.3 (C2) and 167.0 (C7).

Water-soluble sodium salt $Na_3[Au(mna)_2]\cdot 2H_2O$ 4. To 0.506 g (1.00 mmol) of complex **3** suspended in 10 mL water was added 3.0 mL of 1.0 M aqueous NaOH solution (3.00 mmol), followed by filtering through a folded filter paper (Whatman No. 2). The clear yellow filtrate was concentrated to *ca.* 5 mL volume by a rotary evaporator at 50 °C. By slow evaporation from this solution at room temperature for 1 h, clear yellow needle crystals began to form. After 3 days the crystals were collected on a membrane filter (JG 0.2 μm), washed with ethanol (50 mL × 2) and dried *in vacuo* for 2 h, becoming a yellow powder. The relatively light-stable, yellow powder obtained in 0.30 g (51.1%) yield was hygroscopic and soluble in water, but insoluble in most organic solvents {Found: C, 24.62; H, 1.37; N, 5.00. Calc. for $C_{12}H_{10}AuN_2Na_3O_6S_2$ or $Na_3[Au(mna)_2]\cdot 2H_2O$: C, 23.70; H, 1.66; N, 4.61%}. TG/DTA data: weight loss of 5.69% before 197 °C (calc. for 2 H_2O 5.92%); decomposition began gradually around 212 °C with an endothermic peak at 50 °C and exothermic peaks at 212 and 361 °C. Prominent IR bands in the 1800–400 cm^{-1} region (KBr disc): 1598s, 1581s, 1560s, 1456w, 1424m, 1399vs, 1253w, 1055w, 1031w, 839w, 742m, 707m and 653w cm^{-1}. ^1H NMR (25 °C, D_2O): δ 7.36 (1 H, dd, H5, J 5.9), 7.90 (1 H, dd, H4, J 7.3) and 8.18 (1 H, dd, H6, J 4.4 Hz). ^{13}C NMR (25 °C, D_2O): δ 122.2 (C5), 140.6 (C3), 142.8 (C4), 143.6 (C6), 162.4 (C2) and 176.1 (C7).

Compound **4** was also obtained in 41.0% yield (0.41 g scale) by slow evaporation from the aqueous solution of the yellow powder obtained by reaction of $Na[AuCl_4]\cdot 2H_2O : H_2$mna : NaOH = 1 : 4 : 8 in aqueous solution, followed by removing the by-product disulfide (RSSR) of mna^{2-} ligand by a gel filtration (Sephadex G-10, 1.5 × 90 cm). However, the yellow needle crystals obtained by both methods were too small to collect X-ray diffraction data.

Table 3 Crystallographic data for complexes **1** and **3**

	1	**3**
Empirical formula	$C_{36}H_{24}Ag_6N_6O_{12}S_6$	$C_{12}H_9AuN_2O_4S_2$
Formula weight	1572.19	506.30
Crystal system	Triclinic	Trigonal
Space group	$P\bar{1}$ (no. 2)	$R\bar{3}c$ (no. 167)
a/Å	12.958(4)	15.554(3)
b/Å	15.683(3)	
c/Å	11.773(2)	31.260(5)
α/°	103.87(1)	
β/°	102.67(2)	
γ/°	113.47(2)	
V/Å^3	1993(1)	6549(1)
Z	2	16
μ/cm^{-1}	32.72	92.85
R_{int}	0.017	0.069
R	0.040	0.038
R_w	0.057	0.038

X-Ray crystallography

Each single crystal of complexes **1** and **3** sealed in a capillary was used for measurements at room temperature of precise cell constants and intensity data collection on a Rigaku AFC5S diffractometer (Mo-Kα radiation, $\lambda = 0.71069$ Å). The structures were solved by direct methods followed by subsequent Fourier difference calculation and refined by a full-matrix least-squares procedure using the TEXSAN package.[11]

For complex **1**, non-hydrogen atoms except for oxygen atoms in the solvated DMSO were refined anisotropically and hydrogen atoms and oxygen atoms in the solvated DMSO refined isotropically. For **3**, all atoms except hydrogen were refined anisotropically and hydrogen atoms isotropically. In the final Fourier synthesis the electron density fluctuated in the range 0.99 to −0.82 e Å^{-3} for **1** and 1.31 to −1.13 e Å^{-3} for **3**. Crystal data, data collection and refinement are summarized in Table 3.

CCDC reference number 186/1981.

See http//www.rsc.org/suppdata/dt/b0/b001664k/ for crystallographic files in .cif format.

Antimicrobial activity

Antimicrobial activities of the silver(I) and gold(I) compounds prepared here were estimated by the minimum inhibitory concentration (MIC: μg mL^{-1}) as usual.[6k–n]

Bacteria were inoculated into 5 mL of liquid medium (Soybean Casein Digest (SCD) medium) and cultured for 24 h at 35 °C. Yeast were inoculated into 5 mL of liquid medium (Glucose Peptone (GP) medium) and cultured for 48 h at 30 °C. The cultured fluids were diluted, adjusted to the concentration of 10^6–10^7 mL^{-1} and used for inoculation in the MIC test. As for the mold culture, the agar slant (Potato Dextrose (PD) agar medium) for one week cultivation at 27 °C was gently washed with saline containing 0.05% Tween 80. The spore suspension obtained was adjusted to the concentration of 10^6 mL^{-1} and used for inoculation in the MIC test.

The test materials, complexes **1**–**4** and the "free" ligand were dissolved or suspended in water. Such solutions were then diluted with SCD medium for bacteria and with GP medium for yeast and mold. Using these two-fold diluted solutions with concentrations of 1000 to 2 μg mL^{-1} were prepared. Each 1 mL of culture medium containing various concentrations of test materials was inoculated with 0.1 mL of the microorganism suspension prepared above.

Bacteria were cultured for 24 h at 35 °C, yeast for 48 h at 30 °C, and mold for one week at 25 °C, then the growth of microorganisms was observed. When no growth was observed in the medium containing the lowest concentration of test materials the MIC was defined at this point of dilution.

SCD, GP and PD media were purchased from Nissui.

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