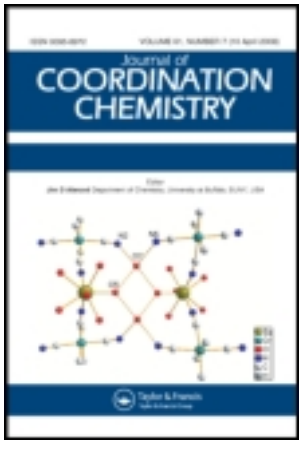

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Synthesis, characterization, and antibacterial activity of two silver(I) compounds with 4-dimethylaminopyridine

Yuguang Li [a], Xiongwei Dong [a], Yi Gou [a], Zhong Jiang [a] & Hai-Liang Zhu [a]

[a] School of Chemistry and Chemical Engineering, Engineering Research Center for Clean Production of Textile Printing, Ministry of Education, Wuhan Textile University, Wuhan 430073, People's Republic of China

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Synthesis, characterization, and antibacterial activity of two silver(I) compounds with 4-dimethylaminopyridine

YUGUANG LI*, XIONGWEI DONG, YI GOU, ZHONG JIANG and HAI-LIANG ZHU*

School of Chemistry and Chemical Engineering, Engineering Research Center for Clean Production of Textile Printing, Ministry of Education, Wuhan Textile University, Wuhan 430073, People's Republic of China

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Two new silver(I) compounds, $[Ag(4\text{-dmapy})_2(p\text{-bromophenylacetate})]\cdot H_2O$ (**1**) and $[Ag(4\text{-dmapy})_2(p\text{-hydroxyphenylacetate})]\cdot 2H_2O$ (**2**) (4-dmapy = 4-dimethylaminopyridine), have been synthesized and characterized. X-ray crystallographic analysis reveals that **1** and **2** contain a linear $Ag(4\text{-dmapy})_2$ chromophore, which further forms dimeric silver(I) units *via* weak silver–silver interaction. The short Ag···Ag separations in **1** and **2** are 3.0395(12) and 3.2697(10) Å, respectively. Compounds **1** and **2** have good anti-*Bacillus subtilis* activity *in vitro* (minimum inhibitory concentration, MIC = 12.5 μg mL^{-1}) but were inactive against *Staphylococcus aureus* and *Escherichia coli* (MIC > 50 μg mL^{-1}).

Keywords: Silver(I) compounds; 4-Dimethylaminopyridine; Crystal structures; Antibacterial activity

1. Introduction

Silver(I) complexes with pyridines and carboxylates have fascinating architectures, supramolecular chemistry, and crystal engineering [1–6], and because of their antimicrobial and antifungal properties they are used in biological and pharmacological chemistry [7–9]. Among applications of silver(I) complexes as functional materials, Ag-based antiseptic materials may have far less propensity to induce microbial resistance than antibiotics [10]. In addition, silver(I) has remarkably low human toxicity compared to other heavy metal ions [11]. For this reason, design of silver(I) complexes with antimicrobial and antifungal activities is an intriguing aspect of bioinorganic chemistry of metal-based drugs.

Silver(I) complexes have a variety of noteworthy antimicrobial activities, although modes of action and mechanism of their antimicrobial activities have not been clarified. It was suggested that one of the key factors determining antibacterial effects of silver(I) complexes is the nature of the atom coordinated to silver(I) and its bonding properties, i.e., the ease of ligand replacement, rather than the solubility, charge, chirality, or

*Corresponding authors. Email: liyg2010@wtu.edu.cn; hlzhu@wtu.edu.cn

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degree of polymerization of the compounds [12–14]. Our previous work focused on the synthesis and therapeutic applications of a series of silver(I) complexes with carboxylic acid derivatives [15–18]. Currently, our group is particularly interested in understanding the activity of such silver(I) complexes with respect to chemical composition, nano-structuring, and anti-microbial activity. In this article, we report the synthesis, structures, and antimicrobial activities of two new silver(I) compounds with 4-dimethylaminopyridine (4-dmapy), [Ag(4-dmapy)$_2$(*p*-bromophenylacetate)] · H_2O (**1**), and [Ag(4-dmapy)$_2$(*p*-hydroxyphenylacetate)]·2H_2O (**2**).

2. Experimental

2.1. *Materials and physical measurements*

All chemicals used in the synthesis were of reagent grade and used without purification. Distilled water was used for all procedures. All experiments were performed at ambient temperature. Elemental analyses (C, H, and N) were performed in an Elementar vario EL III elemental analyzer. IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets from 4000 to 400 cm^{-1}.

2.2. *Synthesis of [Ag(4-dmapy)$_2$(p-bromophenylacetate)] · H_2O (1)*

Compound **1** was prepared by the reaction of Ag_2O (116 mg, 0.5 mmol) with *p*-bromophenylacetic acid (215 mg, 1.0 mmol) in 28% aqueous ammonia (10 mL), and the mixture was stirred for *ca* 15 min until a clear solution was obtained. Then, 4-dimethylaminopyridine (122 mg, 1.0 mmol) was added and the mixture was stirred at room temperature for 20 min to give a colorless clear solution. The resulting solution was kept in air for 7 days with ammonia escaping and crystals of **1** forming at the bottom of the vessel. Colorless crystals were collected and washed with water, and then dried in a vacuum desiccator with $CaCl_2$ (yield 55%). Anal. Calcd for $C_{22}H_{28}AgBrN_4O_3$: C, 45.22; H, 4.83; and N, 9.59%. Found: C, 45.63; H, 4.99; and N, 9.38%. IR data (cm^{-1}, KBr pellets): 3415 vs, 2920 m, 1611 vs, 1482 s, 1383 m, 1227 vs, 1099 m, 1006 s, 1000 w, 805 vs, 692 w, 548 m, and 481 w.

2.3. *Synthesis of [Ag(4-dmapy)$_2$(p-hydroxyphenylacetate)] · 2H_2O (2)*

In a procedure similar to the one needed for the preparation of 1, *p*-hydroxyphenylacetic acid (152 mg, 1.0 mmol) and 4-dimethylaminopyridine (122 mg, 1.0 mmol) are used. Colorless crystals of **2** were collected and washed with water, and then dried in a vacuum desiccator with $CaCl_2$ (yield 49%). Anal. Calcd for $C_{22}H_{31}AgN_4O_5$: C, 48.99; H, 5.79; and N, 10.39%. Found: C, 48.75; H, 5.66; and N, 10.14%. IR data (cm^{-1}, KBr pellets): 3434 m, 3217 vs, 2850 w, 1601 vs, 1563 vs, 1379 m, 1228 vs, 1123 w, 1007 m, 806 s, 687 w, 623 m, 546 m, and 463 w.

2.4. *Crystal structure determinations*

X-ray crystallographic data [19] were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The collected data were reduced using SAINT and empirical absorption corrections were performed using SADABS. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares using the SHELXTL version 5.1. All non-hydrogen atoms were refined anisotropically. All hydrogens were placed in geometrically ideal positions and constrained to ride on their parent atoms. The crystallographic data for **1** and **2** are summarized in table 1.

2.5. *Antibacterial screening method*

The antibacterial activities of the title compounds were tested against *Bacillus subtilis* ATCC 6633, *Staphylococcus aureus* ATCC 6538, *Pseudomonas aeruginosa* ATCC 13525, and *Escherichia coli* ATCC 35218 using Muellere-Hinton (MH) medium (MH medium: casein hydrolysate 17.5 g, soluble starch 1.5 g, beef extract 1000 mL) by 3-(4,5-dimethyl-2-triazyl)-2,5-diphenyl-2H-tetrazolium bromide (MTT) method. The minimum inhibitory concentrations (MICs) of the tested compounds were determined by a colorimetric method using the dye MTT [20]. This yellow tetrazolium salt is cleaved by dehydrogenases inside mitochondria or in other cellular locations possessing dehydrogenase activity to form its purple formazan derivative [21, 22], which can be measured spectrophotometrically at 550 nm. MTT is cleaved by all living, metabolically active microorganisms impendent of proliferation and irrespective of unicellular or multicellular growth, and thus it is a measure of metabolic activity.

A stock solution of the synthesized compound (50 μg mL^{-1}) in DMSO was prepared and graded quantities of the tested compounds were incorporated in a specified quantity of sterilized liquid medium (MH medium for antibacterial activity). A specified

Table 1. Crystal data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{22}H_{28}AgBrN_4O_6$	$C_{22}H_{31}AgN_4O_5$
Molecular weight	584.25	539.38
Temperature (K)	291(2)	291(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	14.3211(15)	13.136(5)
b	9.6562(10)	13.051(5)
c	19.1606(19)	19.038(5)
β	114.851(7)	132.418(17)
Volume (Å^3), *Z*	2404.3(4), 2	2409.5(14), 4
Calculated density (g cm^{-3})	1.614	1.487
Absorption coefficient (mm^{-1})	2.530	0.875
F(000)	1176	1112
θ range for data collection (°)	1.57–26.50	2.10–26.50
Data/restraints/parameters	4960/0/284	4971/6/310
Goodness-of-fit on F^2	1.009	1.002
R_1, wR_2 [$I > 2\sigma(I)$]	0.0606, 0.1452	0.0334, 0.0870

quantity of the medium containing the compound was poured into microtitration plates. Suspension of the microorganism containing approximately 10^5 cfu mL^{-1} was prepared and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37°C for 24 h. After the MICs were visually determined on each of the microtitration plates, 50 mL of PBS (phosphate buffered saline 0.01 mol L^{-1}, pH 7.0, $Na_2HPO_4 \cdot 12H_2O$ (2.9 g), KH_2PO_4 (0.2 g), NaCl (8.0 g), KCl (0.2 g), and distilled water (1000 mL)) containing 2 mg of MTT mL^{-1} was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed and 100 mL of isopropanol containing 5% 1 mol L^{-1} HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density (OD) was measured with a microplate reader at 550 nm. The OD of the blank, which consisted of an uninoculated plate incubated together with the inoculated plates, was subtracted from the ODs of the inoculated plates. The percentage of MTT conversion to its formazan derivative for each well was calculated by comparing the OD at 550 nm (OD_{550}) of the wells with that of the drug-free control based on the following equation: (A_{550} of wells that contained the drug/A_{550} of the drug-free well) × 100%. Growth inhibition was then assessed by the visual observation of the wells containing MTT and compared with the MTT-free wells.

3. Results and discussion

3.1. *Crystal structure descriptions*

[Ag(4-dmapy)$_2$(*p*-bromophenylacetate)]·H_2O (**1**). The X-ray crystal structure of **1** is shown in figure 1. Compound **1** consists of a linear $[Ag(4\text{-dmapy})_2]^+$, a *p*-bromophenylacetate counter-anion and a lattice water molecule. Each silver(I) is coordinated by two nitrogens from two 4-dmapy ligands with Ag–N distances of 2.146(5) and 2.133(5) Å, comparable to that of 2.119(5)–2.159(5) Å previously reported in analogous silver(I) complexes [23, 24]. The pyridyl rings of the 4-dmapy ligands possess perfect planarity, and the dihedral angle of two 4-dmapy molecular planes is 12.8°. In **1**, the carboxylic acid of *p*-bromophenylacetic acid is deprotonated, but the *p*-bromophenylacetate does not coordinate to Ag(I). Unexpectedly, there are weak interactions between silver(I) ion and the deprotonated carboxylate with Ag···O distances of 2.751–3.026 Å, shorter than the sum of van der Waals radii of Ag(I) ion and oxygen [25].

Two linear $[Ag(4\text{-dmapy})_2]^+$ cations in **1** produce one dimeric silver(I) unit with a distorted H-shape coordination sphere *via* weak silver–silver interaction. The Ag–Ag interactions in **1**, Ag–Ag = 3.0395(12) Å, are longer than Ag–Ag distances in similar dinuclear complexes (i.e., 2.8463(4), 2.997(2), and 2.8629(6) Å) [26–28] and slightly shorter than those in the polymeric structure [29–31]. These relatively short Ag–Ag bonds may be considered only as $d^{10}\cdots d^{10}$ noncovalent interactions [32, 33]. Thus, **1** contains silver with three-fold coordination and a $ON_2Ag\cdots AgN_2O$ coordination environment. These dimeric silver(I) units are further linked by weak O–H···O hydrogen bonds between lattice water molecule and carboxylates of *p*-bromophenylacetate with O···O distances of 2.909(10) and 3.027(11) Å to produce a 2-D supramolecular structure (figure 2, table 2). The dimeric silver(I) cations

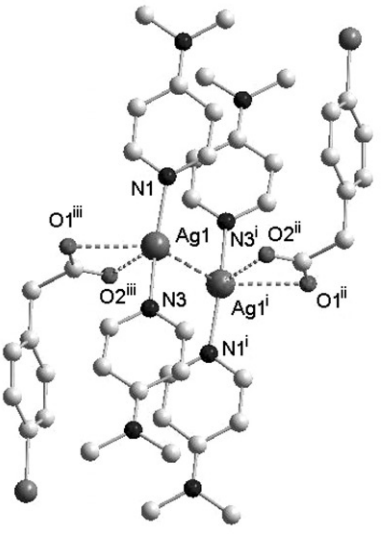

Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Ag1–N1 2.146(5), Ag1–N3 2.133(5), Ag1···O1^{iii} 2.751(5), Ag1···O2^{iii} 3.026(5), Ag1···Ag1^{i} 3.0395(12), N1–Ag1–N3 163.4(2) (symmetry codes: $^{i}1-x, 1-y, -z$; $^{ii}x, 1/2-y, -1/2+z$; $^{iii}1-x, 1/2+y, 1/2-z$).

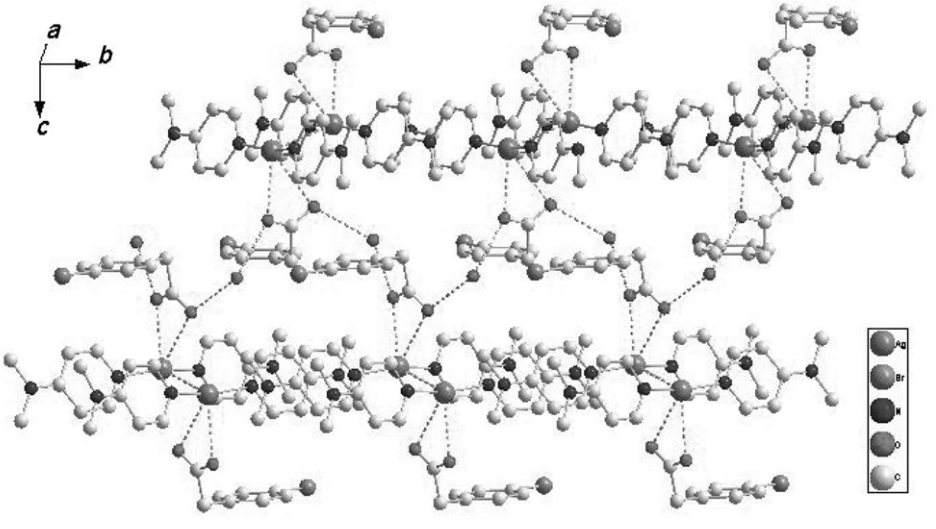

Figure 2. The molecular packing of **1**, together with lattice water molecule.

($[Ag_2(4\text{-dmapy})_4]^{2+}$) behave as the basic silver(I) units to form a "metal compound sandwich layer." Because of the presence of a great number of such weak O–H···O hydrogen bonds, lattice water molecules bridge to generate the one-dimensional (1-D) chains that enhance the structural stability of **1**.

$[Ag(4\text{-dmapy})_2(p\text{-hydroxyphenylacetate})]\cdot 2H_2O$ (**2**). Similar to **1**, compound **2** contains a linear $[Ag(4\text{-dmapy})_2]^{+}$ cation (figure 3) with silver(I) also coordinated by

Table 2. Hydrogen bonds in **1** and **2** (Å, °).

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
1				
O3–H3B···O1	0.85	2.50	2.909(10)	110.9
O3–H3A···O2^{i}	0.85	2.59	3.027(11)	112.8
2				
O3–H3···O4^{i}	0.82	1.85	2.667(3)	176.2
O4–H4A···O2	0.85	1.87	2.715(3)	175.9
O4–H4B···O5^{ii}	0.83	2.01	2.802(4)	157.5
O5–H5A···O1^{iii}	0.83	1.93	2.762(3)	172.1
O5–H5B···O3	0.83	2.13	2.962(4)	171.7

Symmetry codes for **1**: $^{i}1-x, 1/2+y, 3/2-z$. Symmetry codes for **2**: $^{i}1-x, 1-y, 1-z$; $^{ii}x, -1+y, z$; $^{iii}-x, 1/2+y, 1/2-z$

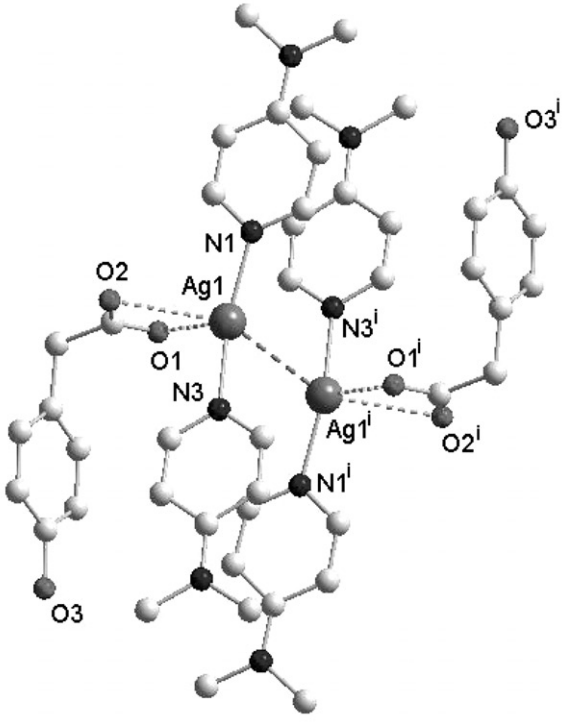

Figure 3. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Ag1–N1 2.141(2), Ag1–N3 2.141(2), Ag1···O1 2.632(5), Ag1···O2 2.805(5), Ag1···Ag1^{i} 3.2697(10), N1–Ag1–N3 160.76(8) (symmetry codes: $^{i}-x, 1-y, 1-z$).

two nitrogens from two 4-dmapy with Ag–N distances of 2.141(2) Å in the normal range of 2.119(5)–2.159(5) Å [23, 24]. The dihedral angle of two 4-dmapy molecular planes connected *via* silver(I) ion is 9.2°, slightly lower than in **1**. In **2**, the deprotonated carboxylate of the *p*-hydroxyphenylacetate also acts as counter-anion. There are weak interactions between silver(I) and the deprotonated carboxylate with the Ag···O

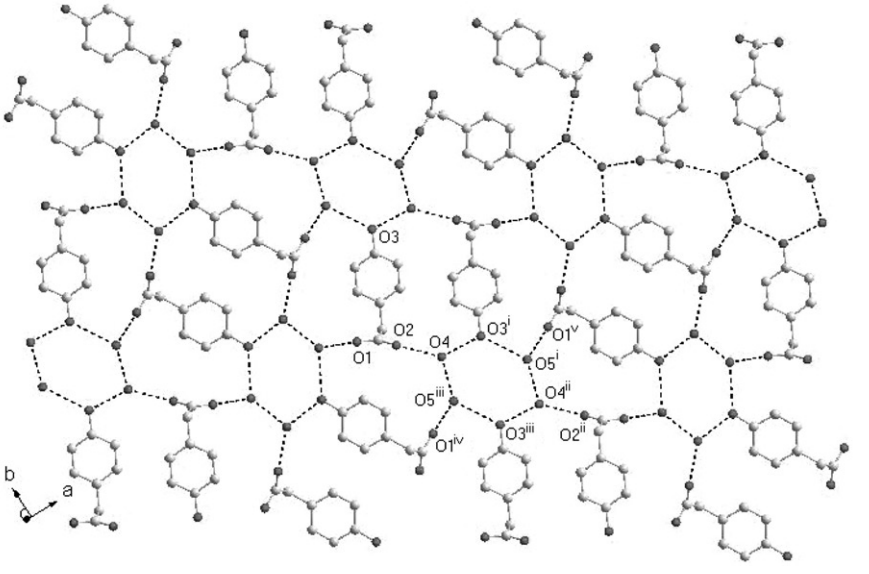

Figure 4. A 2-D layer assembled *via* O–H···O hydrogen bonds in the crystal structure of **2** (symmetry codes: $^{i}1-x, 1-y, 1-z$; $^{ii}1-x, -y, 1-z$; $^{iii}x, -1+y, z$; $^{iv}x, -1/2+y, 1/2-z$; $^{v}1+x, 1/2-y, 1/2+z$).

distances in the range of 2.632–2.805 Å, significantly shorter than the sum of van der Waals radii [25], resulting in the conjugated effect of the deprotonated carboxylate with the C–O distances of the range 1.246(3)–1.248(3) Å.

In **2**, a dimeric silver(I) unit with a distorted H-shape was obtained from two linear $[Ag(4\text{-dmapy})_2]^+$ cations. The Ag–Ag distance (3.2697(10) Å) in $[Ag_2(4\text{-dmapy})_4]^{2+}$ indicates weak Ag···Ag interaction when compared to the van der Waals contact distance (3.40 Å) for Ag–Ag. All the silver(I) ions of **2** have coordination geometry similar to that of Ag in **1**. In contrast, each silver(I) of the dimeric unit in **2** was also linked with two neighboring six-membered rings by the deprotonated carboxylate of *p*-hydroxyphenylacetate with O···O distances of 2.715(3) and 2.762(3) Å. The latter consists of six oxygens from the phenolic hydroxyl of two independent *p*-hydroxyphenylacetates and four lattice water molecules (figure 4, table 2). Three hydrogen bonds are observed in the six-membered rings with O···O···O angles of in the range of 110.57–126.44°. One is a hydrogen bond between the two lattice water molecules with O···O distance of 2.802(4) Å), and the others are between the phenolic hydroxyl of *p*-hydroxyphenylacetate and two lattice water molecules with O···O distances of 2.667(3) and 2.962(4) Å, respectively. This, along with the presence of the weak Ag···Ag interaction, produces a 3-D framework of **2**.

3.2. *IR spectra*

On the basis of the structure and a comparison with spectra of related complexes [34–36], the IR spectra of **1** and **2** have been tentatively assigned. The broadness of $\nu_{(O-H)}$ at 3217–3434 cm^{-1} may be attributed to O–H of lattice water molecule and the

Table 3. MICs of **1** and **2**.

Compounds	MIC ($\mu g\,mL^{-1}$)			
	B. subtilis	*S. aureus*	*P. aeruginosa*	*E. coli*
1	12.5	50	25	50
2	12.5	50	50	50
4-dmapy	>50	>50	>50	>50
p-Bromophenylacetic acid	>50	>50	>50	>50
p-Hydroxyphenylacetic acid	>50	>50	>50	>50
Kanamycin B	–	–	3.125	3.125
Penicillin G	1.562	1.562	–	–

phenolic hydroxyl of *p*-hydroxyphenylacetate. Compounds **1** and **2** show characteristic bands of the deprotonated carboxylate of *p*-bromophenylacetate and *p*-hydroxyphenylacetate: ν_{as}(COO) at 1611 vs, ν_s(COO) at 1383 m, δ(O–C–O) at 692 w for **1**, and ν_{as}(COO) at 1601 vs, ν_s(COO) at 1379 m, and δ(O–C–O) at 687 w for **2**. In addition, the strong band at 1227 and 1228 cm^{-1} assigned to $\nu_{(C-N)}$ in 4-dmapy was shifted to lower wavenumbers in **1** and **2**, and new bands at 548 and 546 cm^{-1} are observed. This may be a stretch of Ag–N [37]. Thus, additional weak bands in the regions of 485–425 and 585–530 cm^{-1} were attributed to $\nu_{(Ag-O)}$ and $\nu_{(Ag-N)}$, respectively [38, 39].

3.3. *Antibacterial activity studies*

Compounds **1** and **2** were evaluated for their antibacterial activities against two Gram-positive bacterial strains (*B. subtilis* and *S. aureus*) and two Gram-negative bacterial strains (*P. aeruginosa* and *E. coli*) by MTT method. The antibacterial activities of the substances, expressed as MIC, are shown in table 3. The three free ligands showed no activity against the four bacteria (MIC > 50 $\mu g\,mL^{-1}$). Both **1** and **2** possess activity against *B. subtilis* with MIC being 12.5 $\mu g\,mL^{-1}$, less active than the positive control penicillin G. Compound **1** shows considerable activity against *P. aeruginosa* with MIC being 25 $\mu g\,mL^{-1}$. In contrast, **2** has no activity against *P. aeruginosa* with MIC being 50 $\mu g\,mL^{-1}$. This may be related to the presence of the different binding site of these silver(I) compounds with the deprotonated carboxylate. The remarkable difference might result from well-established structural differences between fungal and bacterial cells [40], although the exact reasons remain unclear. The actual mechanism of these active silver(I) compounds remains a question to be studied further.

4. Conclusion

Two silver(I) compounds with 4-dimethylaminopyridine are obtained and their crystal structures are reported. This study provides information about the bonding and coordination of silver(I) in the dimeric silver(I) unit ($[Ag_2(4\text{-dmapy})_4]^{2+}$) of **1** and **2**. The antibacterial activities of the synthesized compounds have been studied *in vitro* by

testing them against four bacterial strains. Compounds **1** and **2** exhibited considerable activities against the Gram-positive bacteria *B. subtilis* with MIC being 12.5 μg mL^{-1}.

Supplementary material

CCDC 770642 and 770641 contain the supplementary crystallographic data for **1** and **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@cdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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