Synthesis, crystal structure and *in vitro* antibacterial activity of two novel silver(I) complexes

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ABSTRACT

Two silver(I) complexes $[Ag_2(dppm)_2(L^1)_2(CH_2Cl_2)_2]$ (**1**) and $[Ag_4(dppm)_2(L^2)_2(NO_3)_2]$ (**2**) have been prepared by the reactions of $[Ag_2(dppm)_2(NO_3)_2]$ with HL^1 and HL^2 [dppm = bis(diphenylphosphino)methane, HL^1 = 2-(9H-carbazol-9-yl) acetic acid and HL^2 = (E)-3-(4-(9H-carbazole-9-yl) phenyl) acrylic acid], respectively. Both complexes have been structurally characterized by X-ray crystallography, confirming that **1** is a binuclear complex whereas **2** is a tetranuclear one. Both complexes were assayed for antibacterial activity against two Gram-positive bacterial strains (*Bacillus subtilis* ATCC 6633 and *Staphylococcus aureus* ATCC 6538) and two Gram-negative bacterial strains (*Pseudomonas aeruginosa* ATCC 13525 and *Escherichia coli* ATCC 35218) by MTT method. Complex **2** exhibited powerful antibacterial activities against *B. subtilis* ATCC 6633 with MIC of 0.78 μg/mL, which was superior to the positive controls penicillin G. On the basis of the biological results, structure-activity relationships were discussed.

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1. Introduction

There is considerable interest in the coordination chemistry of silver(I) and gold(I) complexes with biological and pharmacological activity. Studies of gold(I) complexes have focused mostly on their antiarthritic applications and antimicrobial activities [1], while studies of silver(I) complexes have been mainly related to their antimicrobial and antifungal properties [2–4]. However, compared to the number of gold(I) complexes, far fewer silver(I) complexes have been investigated in this connection. On the other hand, the Ag-based antiseptics materials may be linked to far lower propensity to induce microbial resistance than antibiotics [5], and simultaneously remarkably low human toxicity compared to other heavy metal ions [6]. So, the molecular design of such silver(I) complexes are an intriguing aspect of bioinorganic chemistry of metal-based drugs. One approach to such compounds is to combine known biologically benign molecules with suitable donor groups with silver(I) and investigate their properties [7].

One attractive class of ligands comprises carbazole derivatives due to their promising biological activities such as antitumor, antibacterial and so on [8–12]. With this in mind our group are now interested in obtaining silver(I) complexes with carbazole carboxylate ligands as a strategy of preparation of new potential antibacterial candidates in which the metal and the ligand could act synergistically.

Herein, we reported the synthesis, structure, and antibacterial activities of two novel silver(I) complexes of formulates $[Ag_2(dppm)_2L_2^1(CH_2Cl_2)_2]$ (**1**) and $[Ag_4(dppm)_2L_2^2(NO_3)_2]$ (**2**) as single crystals [dppm = bis(diphenylphosphino)methane, HL^1 = 2-(9H-carbazol-9-yl) acetic acid and HL^2 = (E)-3-(4-(9H-carbazole-9-yl) phenyl) acrylic acid]. Preliminary testing of the complexes against two Gram-positive bacterial strains (*Bacillus subtilis* ATCC 6633 and *Staphylococcus aureus* ATCC 6538) and two Gram-negative bacterial strains (*Pseudomonas aeruginosa* ATCC 13525 and *Escherichia coli* ATCC 35218) was performed *in vitro*. Both complexes showed potent antibacterial activity against the four bacterial strains. Most importantly, complex **2** showed powerful antibacterial activity against *B. subtilis* ATCC 6633 with MIC of 0.78 μg/mL, which was superior to the positive control penicillin G. On the basis of the results, the structure-activity relationships (SAR) were discussed.

2. Experimental

2.1. Materials and methods

The products employed in the present study were used as received, unless otherwise stated, and used without further

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purification except methanol, which was distilled over natrium. The ligands 2-(9H-carbazol-9-yl) acetic acid (HL[1]) and (E)-3-(4-(9H-carbazole-9-yl) phenyl) acrylic acid (HL[2]) were synthesized as previously reported [13,14], see Scheme 1. Carbon, hydrogen and nitrogen assays were carried out with a CHN–O-Rapid instrument and were within ±0.4% of the theoretical values. IR spectra were record on a Nicolet 470 FT-IR spectrophotometer using KBr discs in the range 4000–400 cm^{-1}.

2.2. Synthesis of the complexes 1 and 2

The complexes were obtained by reacting the $[Ag_2(dppm)_2(NO_3)_2]$ [15] (1 mmol) with the proper ligand (1 mmol) in methanol, respectively, as below specified.

$[Ag_2(dppm)_2(L^1)_2(CH_2Cl_2)_2]$ (1): To a suspension of $[Ag_2(dppm)_2(NO_3)_2]$ (1.108 g, 1 mmol) in 25 mL methanol was added HL[1] (0.225 g, 1 mmol). The reaction mixture was heated under reflux for 30 min, and then allowed to cool to room temperature. The solution was filtered to afford the targeting complex as white powder (1.44 g, 90%). Single crystals of complex 1 were obtained by evaporating slowly in dichloromethane/ethyl ether. m.p. 158 °C. Anal. Calc. for $C_{80}H_{68}Ag_2Cl_4N_2O_4P_4$ (1602.85): C, 59.95; H, 4.28; N, 1.75. Found: C, 60.10; H, 4.29; N, 1.74%. IR (KBr, cm^{-1}): 1603 (m), 1486 (m), 1433 (s), 1201 (w), 1140 (w), 1097 (m), 1023 (w), 996 (w), 776 (m), 735 (s), 692 (s).

$[Ag_4(dppm)_2(L^2)_2(NO_3)_2]$ (2): To a suspension of $[Ag_2(dppm)_2(NO_3)_2]$ (1.108 g, 1 mmol) in 25 mL methanol was added HL[2] (0.313 g, 1 mmol). The reaction mixture was heated under reflux for 30 min, and then allowed to cool to room temperature. The solution was filtered to afford the targeting complex as white powder (1.72 g, 88%). Single crystals of complex 2 were obtained by evaporating slowly in dichloromethane/ethyl ether. m.p. 187 °C. Anal. Calc. for $C_{92}H_{72}Ag_4N_4O_{10}P_4$ (1948.94): C, 56.70; H, 3.72; N, 2.87. Found: C, 56.47; H, 3.73; N, 2.88%. IR (KBr, cm^{-1}): 1601 (m), 1548 (m), 1514 (m), 1451 (m), 1384 (s), 1360 (s), 1336 (m), 1228 (m), 1097 (w), 739 (m), 694 (m), 518 (w), 476 (w).

2.3. X-ray crystallography

The crystallographic data for 1 and 2 were collected on a Bruker Smart 1000 CCD area detector diffractometer. Equipped with Mo Kα (λ = 0.71073 Å) radiation using ω-scan mode. Empirical absorption correction was applied to the data. The structures were solved by direct methods and refined by full-matrix least-squares methods on F [2]. All non-hydrogen atoms were located from the trial structure and then refined anisotropically. All hydrogen atoms were generated in idealized positions. All calculations were performed with SHELXL-97 programs. Other relevant parameters of the crystal structure are listed in Table 1.

Table 1
Crystallographic data and structure refinements for complexes 1 and 2.

Compound	1	2
Formula	$C_{80}H_{68}Ag_2Cl_4N_2O_4P_4$	$C_{92}H_{72}Ag_4N_4O_{10}P_4$
Formula weight	1602.78	1948.90
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Crystal size (mm^3)	0.49 × 0.47 × 0.46	0.84 × 0.33 × 0.19
a (Å)	10.9700(14)	10.081(5)
b (Å)	11.8900(15)	22.826(5)
c (Å)	14.240(2)	17.715(5)
α (°)	104.120(3)	90.000(5)
β (°)	95.350(2)	101.759(5)
γ (°)	100.350(3)	90.000(5)
Volume (Å^3)	1753.6(4)	3991(2)
Z	1	2
D_c (g/cm^{-3})	1.518	1.622
μ (mm^{-1})	0.856	1.112
$F(0\,0\,0)$	816	1960
θ rang (°)	1.49–25.01	2.065–29.26
Reflections collected	8462	39720
Reflections unique	5895	10 175
Parameters	433	514
Goodness-of-fit (GOF) on F^2	1.015	0.844
R_1, wR_2 [$I > 2\sigma(I)$]	0.0684, 0.1589	0.0335, 0.1063
R_1, wR_2 [all data]	0.1227, 0.1998	0.0515, 0.1249

2.4. Antibacterial activity

The antibacterial activities of the synthesized complexes were tested against B. subtilis ATCC 6633, E. coli ATCC 35218, P. aeruginosa ATCC 13525 and S. aureus ATCC 6538 using MH medium (Muellere-Hinton medium: casein hydrolysate 17.5 g, soluble starch 1.5 g, beef extract 1000 mL) by MTT method. The MICs of the tested compounds were determined by a colorimetric method using the dye 3-(4,5-dimethyl-2-triazyl)-2,5-diphenyl-2H-tetrazolium bromide (MTT) [16]. This yellow tetrazolium salt is cleaved by dehydrogenases inside mitochondria or in other cellular locations possessing dehydrogenase activity to form its purple formazan derivative [17,18], 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 is a measure of metabolic activity.

A stock solution of the synthesized compound (50 μg/mL) in DMSO was prepared and graded quantities of the tested compounds were incorporated in specified quantity of sterilized liquid medium (MH medium for antibacterial activity). A specified quantity of the medium containing the compound was poured into microtitration plates. Suspension of the microorganism was prepared to contain approximately 10^5 cfu/mL and applied to microtitration
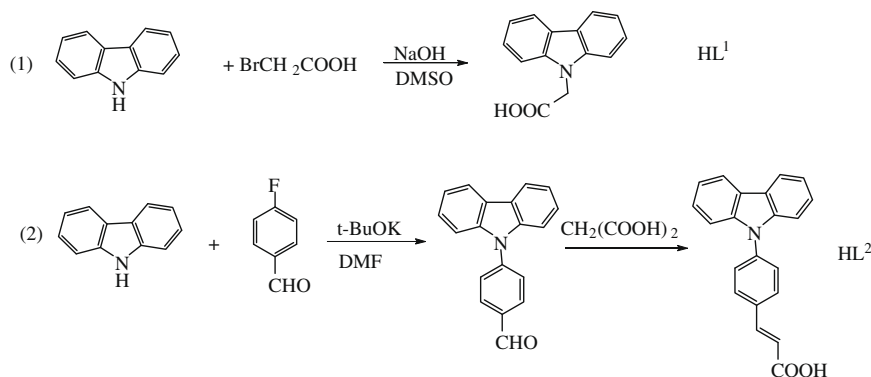
Scheme 1.

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, pH 7.4, $Na_2HPO_4 \cdot 12H_2O$ (2.9 g), KH_2PO_4 (0.2 g), NaCl (8.0 g), KCl (0.2 g), distilled water (1000 mL) containing 2 mg of MTT/mL 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 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 then was assessed by visual observation of the wells containing MTT and compared with the MTT-free wells.

The observed MICs are presented in Table 4. The experiment has been done in triplicate and the results were averaged.

3. Results and discussion

3.1. Structural studies

Ag(I) has preference for a linear coordination, likely because it has s- and p-orbitals available for bonding. However, also due to the symmetric d^{10} character, a substantial number of coordination numbers and geometries have been obtained. Thus, it can also bind bidentate ligands to form one-dimensional polymeric chains, as well as di- and polynuclear complexes.

The molecular structures of complexes **1** and **2** with the atom numbering scheme are depicted in Figs. 3 and 4, respectively. Selected bond lengths and angles with their estimated standard deviations are listed in Tables 2 and 3.

$[Ag_2(dppm)_2(L^1)_2(CH_2Cl_2)_2]$ (**1**) crystallizes as a binuclear complex in the triclinic space group $P\bar{1}$. The molecular structure consists of a neutral dimeric molecular unit with the two silver atoms bridged by a pair of dppm molecules, see Fig. 1. The complex has two equivalent L^1, two carbazole planes of L^1 possess perfect planarity and two C–O bond lengths of L^1 are 1.232 Å and 1.229 Å. Two molecules of dppm are also equivalent in the complex with the same bond lengths and same dihedral angles between phenyl rings. In addition, each silver atom is terminally bound by a single ligand (L^1) in the monodentate coordination mode. Hence, each silver atom is tricoordinate with a coordination sphere of P, 2O.

$[Ag_4(dppm)_2(L^2)_2(NO_3)_2]$ (**2**) crystallizes as a tetranuclear complex in the monoclinic space group $P2_1/c$. The tetranuclear complex, which consists of two $[Ag_2(dppm)L^2(NO_3)]$ subunits bound together by two Ag–O bonds [Ag(2)–O(4)], is a ladder framework supported by a central four-membered Ag_2O_2 ring, see Fig. 2. The complex has two equivalent ligands (L^2) and both the carboxyl

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**.

Bond lengths			
Ag1–O1	2.328 (5)	Ag1–P1	2.403 (18)
Ag1–P2A	2.4238(19)	Ag1–Ag1A	3.2277(12)
Bond angles			
O1–C1–O2	127.7(8)	O1–Ag1–P1	108.16 (15)
O1–Ag1–P2A	98.75(15)	P1–Ag1–Ag1A	90.64(5)
P1–C15–P2	112.5(3)	O1–Ag1–Ag1A	136.77(18)

Table 3
Selected bond lengths (Å) and angles (°) for complex **2**.

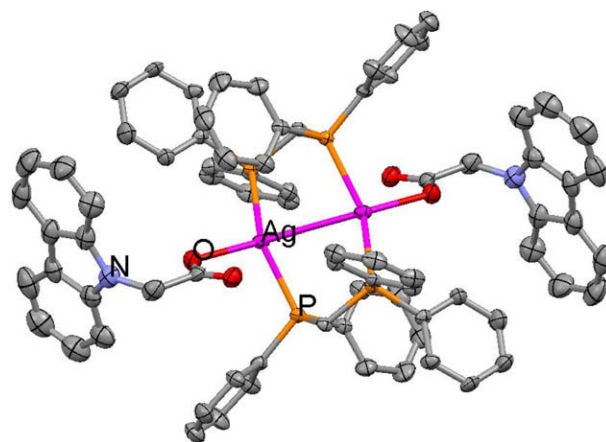| Bond lengths			
Ag1–O1	2.327(3)	Ag1–O5	2.2167(18)
Ag1–P1	2.3395(10)	Ag2–O2	2.718 (2)
Ag2–O4	2.2772(17)	Ag2–P2	2.3619(11)
Ag1–Ag2	2.9258(7)		
Bond angles			
P1–Ag1–O5	134.15(6)	P1–Ag1–Ag2	94.952(19)
Ag2–Ag1–O5	82.61(5)	O1–Ag1–O5	93.31(9)
O1–Ag1–Ag2	101.75(6)	O1–Ag1–P1	131.49(8)
P2–Ag2–Ag1	87.973(19)	P2–Ag2–O4A	128.23(5)
O2–Ag2–O4	85.66 (3)	O2–Ag2–Ag1	60.08 (6)
O2–Ag2–P2	120.51 (1)	P2–C46–P1	112.00(13)
Ag1–Ag2–O4	76.68(4)		

Fig. 1. Molecular structure of the complex **1** (all hydrogen atoms and two CH_2Cl_2 molecules have been omitted for clarity) with 30% probability ellipsoids.

groups of them are in bidentate coordination mode with three silver atoms. The complex also has two nitrate bonding to the two exocyclic silver atoms [Ag(1), Ag(1)A], which is remarkable different from complex **1**. Hence, the two exocyclic Ag-atoms [Ag(1)] and the two endocyclic Ag-atoms [Ag(2)] all have four-coordination mode with a P, 3O coordination environment. Two carbazole planes of L^2 possess perfect planarity and two C–O bond lengths of L^2 are 1.264 Å and 1.241 Å. The dihedral angle between carbazole and phenyl ring is 44.28°. Two molecules of dppm are also equivalent in the complex with the same bond lengths and same dihedral angles between phenyl rings. Furthermore, The Ag(1)–Ag(2) distance of 2.9258(7) Å, which is nearly equal to that in
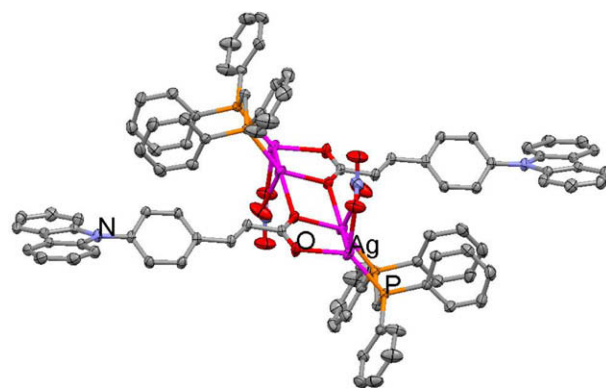

Fig. 2. Molecular structure of complex **2** (all hydrogen atoms have been omitted for clarity) with 30% probability ellipsoids.
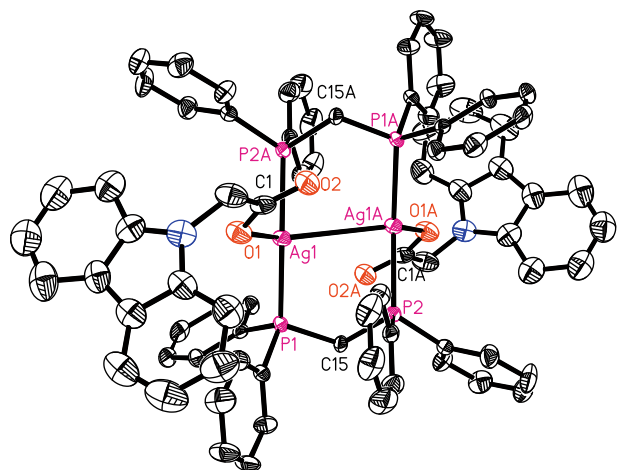
Fig. 3. ORTEP drawing of complex **1** with the atom numbering scheme (all hydrogen atoms and two CH_2Cl_2 molecules have been omitted for clarity).
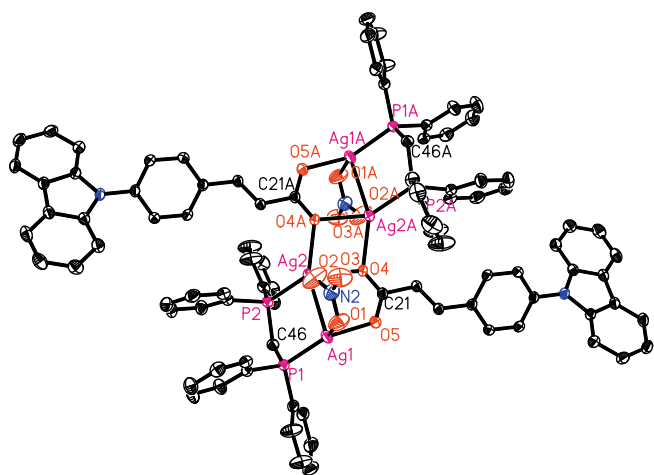

Fig. 4. ORTEP drawing of complex **2** with the atom numbering scheme (all hydrogen atoms have been omitted for clarity).

metallic silver (2.89 Å), indicating the existence of weak metal–metal interactions [19,20] between them. On the other hand, the Ag(2)–O(2) distance of 2.718(2) Å is longer than Ag(1)–O(1), Ag(1)–O(5) and Ag(2)–O(4) distances; of 2.327(3), 2.2167(18) and 2.2772(17) Å, respectively. This bond distance is longer than normally observed in related complexes.

3.2. Antibacterial activity

The two complexes prepared were evaluated for their antibacterial activities against two Gram-positive bacterial strains (*B. subtilis* ATCC 6633 and *S. aureus* ATCC 6538) and two Gram-negative bacterial strains (*E. coli* ATCC 35218 and *P. aeruginosa* ATCC 13525) by MTT method. The antibacterial activities of the substances, expressed as minimum inhibitory concentration, are shown in Table 4.

Antibacterial activities of the two "free" ligands were estimated as >50 μg/mL for the four bacterial (*B. subtilis* ATCC 6633, *S. aureus* ATCC 6538, *E. coli* ATCC 35218, *P. aeruginosa* ATCC 13525), showing a lack of activity against all test bacterial.

Silver(I) complexes have shown a variety of noteworthy antimicrobial activities, although mode of action and mechanism of their antimicrobial activities have not been clarified. It was suggested

Table 4
MICs of the synthesized compounds.

Compound	Minimum inhibitory concentrations (μg/mL)			
	A	B	C	D
1	6.25	25	12.5	25
2	0.78	6.25	6.25	12.5
HL^1	>50	>50	>50	>50
HL^2	>50	>50	>50	>50
[Ag$_2$(dppm)$_2$(NO$_3$)$_2$]	25	>50	50	25
Kanamycin B	/	/	3.125	3.125
Penicillin G	1.562	1.562	/	/

Note: A, *Bacillus subtilis* ATCC 6633; B, *Staphylococcus aureus* ATCC 6538; C, *Pseudomonas aeruginosa* ATCC 13525; D, *Escherichia coli* ATCC 35218.

that one of the key factors determining the antibacterial effects of silver complexes is the nature of the atom coordinated to silver(I) atom and its bonding properties, *i.e.* the ease of ligand replacement, rather than the solubility, charge, chirality, or degree of polymerization of the complexes [1,3]. Thus, it is reasonable that **1** and **2** with the weaker Ag(I)–O bonds show a wider spectrum of antibacterial activities against the four test strains, because the further ligand replacement with biological ligands is possible. In contrast, almost all compounds with Ag(I)–P bonds investigated thus far have shown no activity against bacterial, yeast, or moulds [21]. Thus, complex [Ag$_2$(dppm)$_2$(NO$_3$)$_2$], which was used as a material in this work, showed almost no antibacterial activity (MIC > 50 μg/mL).

In this work, we have found that both the neutral complex [Ag$_2$(dppm)$_2$(L^1)$_2$(CH$_2$Cl$_2$)$_2$] (**1**) and the cationic complex [Ag$_4$(dppm)$_2$L$_2^2$]$^{2+}$(NO$_3$)$_2$ (**2**) with two nitrate anions show a same spectrum of antibacterial activities. The most remarkable difference is found with the Gram-positive bacterial *B. subtilis* ATCC 6633; the cationic complex with MIC of 0.78 μg/mL, which was superior to the positive controls penicillin G, is more active than the neutral one. Because both complexes are active against the two Gram-negative bacterial *P. aeruginosa* ATCC 13525 and *E. coli* ATCC 35218, the permeability of the outer membrane of the Gram-negative bacterial cannot not be a factor [22]. The result would suggest a mechanism for the antibacterial function, which is determined not only by the structure of the cation and conjugate acid but also by the transport phenomena and by ligand exchange equilibria. It is conceivable that ligand replacement from Ag–O-core cluster to a new Ag–S(biological ligand) complex could occur in the presence of sulfur-containing biological molecules. Thus, it can be suggested that, rather than the geometries of the silver(I) clusters, other factors may account for observed differences in antibacterial activities: factors such as the hydrophobicity or hydrophilicity of the clusters or the ease of ligand exchange between Ag–O cores and Ag–S(biological ligand) bonds. The actual mechanism of these active silver(I) complexes remains a question to be further studied.

As far as structure-activity relationships (SAR) go, we also have no clear indications that the substitution pattern on the carbazole ring is decisive; thus, the stoichiometry and coordination chemistry of the complex may be more important.

4. Conclusion

Two silver(I) complexes have been obtained in the crystalline state, and the structures of them are reported here. This study provides some useful information about the bonding nature and coordination mode in the silver(I) complexes. The *in vitro* antibacterial activities of the synthesized complexes have been studied by testing them in four bacterial strains which shows their inhibitory effect. Complex **2** exhibited powerful antibacterial activities against *B. subtilis* ATCC 6633 with MIC of 0.78 μg/mL, which was superior to the positive controls penicillin G.

Acknowledgements

Appendix A. Supplementary material

CCDC 704787 and 704788 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.04.020.

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