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Synthesis, Crystal Structure, and Antimicrobial Activity of Silver(I) Complexes Derived from 3-Nitrobenzoic Acid and Diamines[1]

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Abstract—Two new silver(I) complexes, $[Ag_2(NBA)_2(DAC)]$ (**I**) and $[Ag_2(NBA)_2(DAB)]$ (**II**), where NBA, DAC, and DAB are 3-nitrobenzoate, 1,2-diaminocyclohexane, and 1,4-diaminobutane, respectively, are prepared and characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction (CCDC nos. 1487698 (**I**), 1487699 (**II**)). The Ag(1) atom in **I** is in a linear coordination mode built by two N atoms from two DAC ligands. The Ag(2) atom in **I** is in a distorted triangular coordination mode formed by three O atoms from two NBA ligands. The Ag(1) atom in **II** is in a linear coordination mode formed by one O atom of a NBA ligand and one N atom of a DAB ligand. Crystal structures of both complexes are stabilized by hydrogen bonds and weak $\pi\cdots\pi$ interactions. The effect of the complexes on the antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* is studied.

Keywords: silver complex, crystal structure, polynuclear complex, antimacrobial activity

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INTRODUCTION

Silver(I) complexes usually adopt coordination numbers from two to six, resulting in their coordination spheres ranging from linear to octahedral. Based on this property, silver chemistry has attracted great interest in recent years to explore the versatility of silver(I) coordination polymers with unusual structures and useful properties [1–4]. The versatile structures, photoluminescence and biological activities of silver complexes are received particular attention [5–9]. It has been demonstrated that silver complexes with Ag–N, Ag–S, or Ag–O bonds have antibacterial activity [10–12] and antitumor activity [13, 14]; these complexes have been widely used to treat a variety of diseases. In recent years, many types of ligands have been used to prepare silver complexes. Organic acids and amines are interesting ligands for the preparation of silver complexes [15–21]. In the present work, two new silver complexes with 3-nitrobenzoate ligand and diamines are reported. They are $[Ag_2(NBA)_2(DAC)]$ (**I**) and $[Ag_2(NBA)_2(DAB)]$ (**II**), where NBA, DAC, and DAB are 3-nitrobenzoate, 1,2-diaminocyclohexane, and 1,4-diaminobutane, respectively.

EXPERIMENTAL

Material and methods. 3-Nitrobenzoic acid, 1,2-diaminocyclohexane, 1,4-diaminobutane, and silver oxide were purchased from Fluka. Other reagents and solvents were of analytical grade and were used without further purification. Elemental (C, H, and N) analyses were made on a Perkin-Elmer Model 240B automatic analyser. IR spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer. X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer.

Synthesis of I. Ag_2O (0.023 g, 0.1 mmol) was suspended in a 30% ammonia solution (15 mL) of 3-nitrobenzoic acid (0.033 g, 0.2 mmol). The suspension was constantly stirred at room temperature until the solid dissolved. Then, 1,2-diaminocyclohexane (0.023 g, 0.2 mmol) dissolved in methanol (2 mL) was added to the mixture. The final mixture was stirred at room temperature for 20 min and filtered. The filtrate was kept still at dark for slow evaporation of the solvent. Colorless crystals suitable for X-ray diffraction of the complex were formed and collected by filtration. Yield, 37%.

For $C_{20}H_{16}N_4O_8Ag_2$

anal. calcd., %:	C, 36.61;	H, 2.46;	N, 8.54.
Found, %:	C, 36.39;	H, 2.54;	N, 8.37.

Synthesis of II. Ag_2O (0.023 g, 0.1 mmol) was suspended in a 30% ammonia solution (15 mL) of 3-nitrobenzoic acid (0.033 g, 0.2 mmol). The suspension was constantly stirred at room temperature until the solid dissolved. Then, 1,4-diaminobutane (0.018 g,

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Table 1. Crystallographic data and structure refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
Molecular weight	662.1	636.1
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	7.0324(6)	4.444(1)
b, Å	10.967(2)	23.529(2)
c, Å	32.268(2)	10.057(2)
β, deg	90.132(2)	91.985(2)
V, Å^3	2488.7(5)	1050.8(3)
Z	4	2
ρ_{calcd}, g cm^{-3}	1.624	2.010
Crystal size, mm	0.21 × 0.19 × 0.17	0.23 × 0.23 × 0.20
μ, mm^{-1}	1.624	1.918
Radiation (λ, Å)	MoK_α (0.71073)	
T_{min}/T_{max}	0.7267/0.7698	0.6667/0.7003
Reflections measured	7555	4429
Index ranges (h, k, l)	$-8 \le h \le 8$, $-12 \le k \le 13$, $-25 \le l \le 39$	$-4 \le h \le 5$, $-26 \le k \le 28$, $-9 \le l \le 12$
θ Range for data collection, deg	2.90–25.50	3.29–25.49
Unique reflections (R_{int})	4375 (0.0329)	1961 (0.0988)
Observed reflections ($I > 2\sigma(I)$)	2354	1417
Parameters/restraints	380/4	145/0
Goodness of fit on F^2	1.043	1.057
R_1, wR_2 ($I \ge 2\sigma(I)$)*	0.0752, 0.2108	0.0548, 0.1170
R_1, wR_2 (all data)*	0.1279, 0.2612	0.0784, 0.1364

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

0.2 mmol) dissolved in methanol (2 mL) was added to the mixture. The final mixture was stirred at room temperature for 20 min and filtered. The filtrate was kept still at dark to slow evaporate of the solvent. Colorless crystals suitable for X-ray diffraction of the complex were formed and collected by filtration. Yield, 45%.

For $C_{18}H_{20}N_4O_8Ag_2$			
anal. calcd., %:	C, 33.99;	H, 3.17;	N, 8.81.
Found, %:	C, 33.82;	H, 3.30;	N, 8.72.

X-ray diffraction. Data were collected from selected crystals mounted on glass fibers. The data for the complexes were processed with SAINT [22] and corrected for absorption using SADABS [23]. Multi-scan absorption corrections were applied with ψ scans [24]. The structures of the complexes were solved by direct method using SHELXS-97 program and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters [25]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at the calculated positions. The cyclohexyl group is disordered over two sites with occupancies of 0.58(3) and 0.42(3). Crystallographic data for the complexes are listed in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material for the structures has been deposited with the cambridge crystallographic data centre (CCDC nos. 1487698 (**I**), 1487699 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

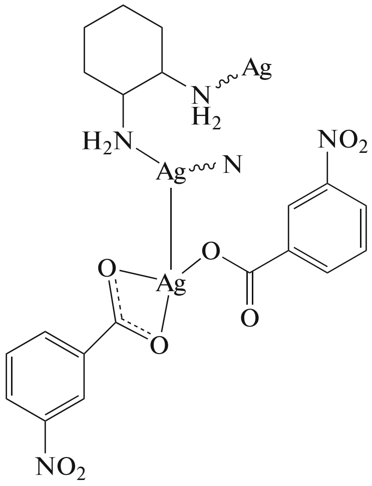
RESULTS AND DISCUSSION

The complexes **I** and **II** were obtained by the reaction of 3-nitrobenzoic acid, silver oxide, and diamines in ammonia solution.

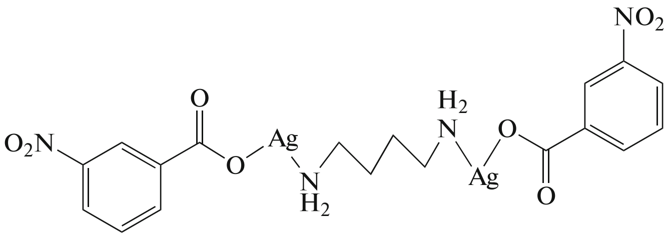
Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I			
Ag(1)–N(1)	2.16(2)	Ag(1)–N(2*A*)	2.19(3)
Ag(2)–O(1)	2.115(8)	Ag2–O(3)	2.376(7)
Ag(2)–O(4)	2.395(8)		
II			
Ag(1)–N(2)	2.133(5)	Ag(1)–O(1)	2.144(4)
Angle	ω, deg	Angle	ω, deg
I			
N(1)Ag(1)N(2*A*)	177.8(7)	O(1)Ag(2)O(3)	148.5(4)
O(1)Ag(2)O(4)	157.0(4)	O(3)Ag(2)O(4)	54.6(3)
II			
N(2)Ag(1)O(1)	174.84(17)		

* Symmetry code: (*A*) 1 + *x*, *y*, *z*.



(I)



(II)

The broad peak at about 3450 cm^{-1} is due to traces of cohesive water. The broad and medium peaks observed for 3-nitrobenzoic acid centered at 1700 cm^{-1} are absent in the silver complexes, which indicates the coordination through the deprotonated carboxylate groups. The typical medium and sharp bands of N–H groups are observed in the range 3100–3300 cm^{-1}. Several peaks in the interval 1600–1430 cm^{-1} are probably due to the C=C and C=N stretching vibrations of the benzene rings. The C–O stretching vibrations of the carboxylate group are located at about 1322 cm^{-1}.

The repeat unit of complex **I** is shown in Fig. 1a. The Ag(1) atom is coordinated by two amino N atoms from 1,2-diaminocyclohexyl groups, forming a linear coordination geometry. The bond angle of 174.9(4)° indicates the deviation from ideal linear geometry. The Ag(2) atom is coordinated by three carboxylate

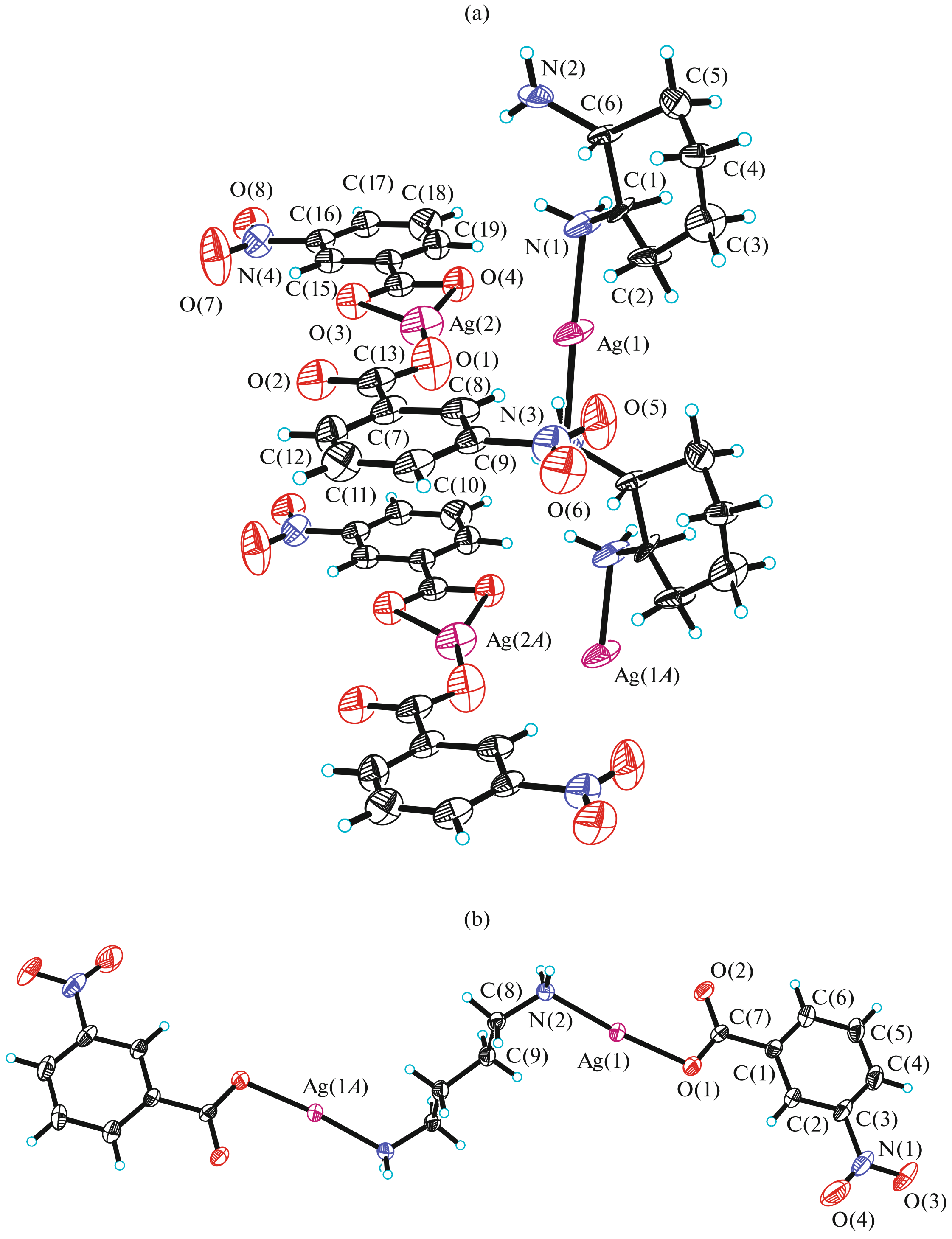


Fig. 1. Molecular structure of complex **I** (a) and **II** (b) at 30% probability displacement. Only the major component of the disordered cyclohexyl group is shown.

O atoms from 3-nitrobenzoate ligands, forming a distorted triangular coordination geometry. The bond angles are range from 54.8(3)° to 156.4(4)°, indicating the deviation from ideal triangular geometry. The Ag(1)···Ag(2) distance is 3.194(2) Å. The coordinate bond lengths are comparable to those observed in sim-

Table 3. Geometric parameters of hydrogen bonds for complexes **I** and **II***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
		I		
N(2)–H(2*D*)···O(2)^{i}	0.90(10)	2.46(7)	2.997(13)	118
N(1)–H(1*A*)···O(2)^{i}	0.90	2.45	2.992(13)	119
		II		
N(2)–H(2*B*)···O(2)^{ii}	0.90	2.15	2.980(6)	152
N(2)–H(2*A*)···O(2)^{ii}	0.90	2.29	3.087(7)	148

* Symmetry codes: ^{i} $-x$, $1-y$, $-z$; ^{ii} $-x$, $-y$, $1-z$.

ilar silver complexes [26–28]. In the crystal structure of the complex, molecules are linked through intermolecular N–H···O hydrogen bonds, to form chains running along the *x* axis (Table 3, Fig. 2a).

The molecule of complex **II** is shown in Fig. 1b. The Ag(1) atom is coordinated by one amino N atom of 1,4-diaminobutane and one carboxylate O atom of 3-nitrobenzoate ligand, forming a linear coordination geometry. The bond angle of 174.8(2)° indicates the deviation from ideal linear geometry. The coordinate bond lengths are similar to those of complex **I**, and comparable to those observed in similar silver complexes [26–28]. In the crystal structure of the complex, molecules are linked through intermolecular N–H···O hydrogen bonds, to form layers parallel to *xz* plane (Fig. 2b).

Qualitative determination of antimicrobial activity was done using the disk diffusion method [29, 30]. The results are summarized in Table 4. A comparative study of minimum inhibitory concentration (MIC) values of 3-nitrobenzoic acid, 1,2-diaminocyclohexane, 1,2-diaminobutane, and the two complexes indicated that the complexes have better activity than the ligands in their free form. Generally, this is caused by the greater lipophilic nature of the complexes than the ligand. Such increased activity of the metal chelates can be explained on the basis of chelating theory [31]. On chelating, the polarity of the metal atoms will be reduced to a greater extent due to the overlap of the

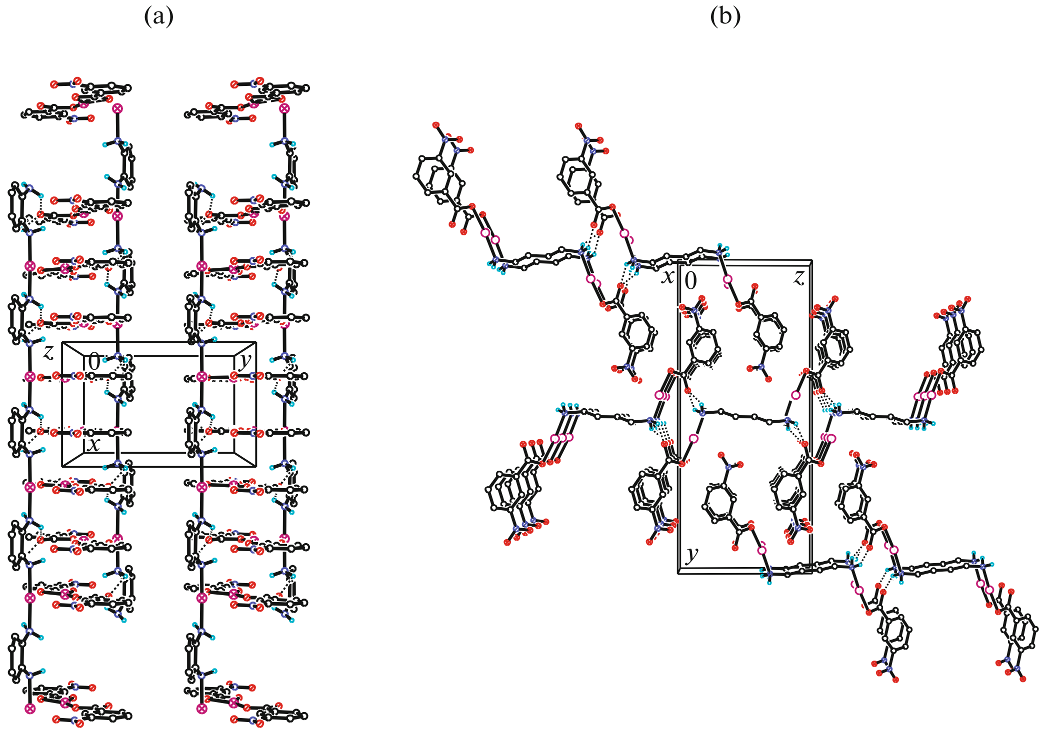


Fig. 2. The hydrogen bonds linked chain structure of complex **I** (a) and layer structure of complex **II** (b).

Table 4. MIC values (μg/mL) for antibacterial activity of the complexes

Compound	*Staphylococcus aureus*	*Escherichia coli*	*Candida albicans*
3-Nitrobenzoic acid	>512	32	>512
1,2-Diaminohexane	64	128	>512
1,4-Diaminobutane	128	32	256
I	0.25	1.0	8.0
II	0.50	1.0	16.0
Tetracycline	0.32	2.12	>512

ligand orbital and partial sharing of positive charge of the metal atoms with donor atoms. Further, it increases the delocalization of *p*-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocks the metal binding sites on enzymes of microorganisms.

From Table 4, it can be seen that the complexes show greater antibacterial and antifungi activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* when compared to the free ligands. The complexes have strong activities against *Staphylococcus aureus* and *Escherichia coli*, which is superior to tetracycline. The complexes also show effective activity against *Candida albicans*, yet the free ligands and tetracycline are negative.

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