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**CRYSTAL STRUCTURES OF TWO NEW DINUCLEAR Ag(I) COMPLEXES
CONSTRUCTED FROM 4,4'-BIPHENYLDICARBOXYLIC ACID
AND N-CONTAINING LIGANDS**© 2011 S.-F. Lou¹, X. Zheng², Y. Chen², X.-Y. Qiu^{2*}¹Department of Public Subject, Shangqiu Medical College, Shangqiu 476000, PR China²Department of Chemistry, Shangqiu Normal University, Shangqiu 476000, PR China

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The reaction of silver 4,4'-biphenyldicarboxylate with 1,3-diaminopropane (DAP) and 2-amino-5-methylpyridine (AMP) respectively results in the formation of two dinuclear silver(I) complexes: $[\text{Ag}_2(\text{DAP})_2](\text{BPC}) \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ag}_2(\text{BPC})(\text{AMP})_4] \cdot 2\text{H}_2\text{O}$ (**2**), where BPC is 4,4'-biphenyldicarboxylate. The complexes are characterized by elemental analysis and X-ray crystallography. Complex **1** crystallizes in the triclinic system, *P*-1 space group, $a = 8.585(2) \text{ \AA}$, $b = 8.849(2) \text{ \AA}$, $c = 9.890(3) \text{ \AA}$, $\alpha = 107.893(3)^\circ$, $\beta = 94.139(3)^\circ$, $\gamma = 113.202(3)^\circ$, $V = 640.9(3) \text{ \AA}^3$, $Z = 1$. Complex **2** crystallizes in the triclinic system, *P*-1 space group, $a = 11.818(3) \text{ \AA}$, $b = 13.132(4) \text{ \AA}$, $c = 13.281(4) \text{ \AA}$, $\alpha = 92.571(4)^\circ$, $\beta = 96.425(3)^\circ$, $\gamma = 102.142(4)^\circ$, $V = 1997.5(10) \text{ \AA}^3$, $Z = 2$. Complex **1** consists of a macrocyclic dinuclear silver(I) dication, a 4,4'-biphenyldicarboxylate anion, and two water molecules of crystallization. Each Ag atom is in a linear coordination. Complex **2** consists of a dinuclear silver(I) complex molecule and two water molecules of crystallization. Each Ag atom is in a T-shaped coordination. The Ag...Ag separations are 5.127(2) Å in **1** and 3.172(2) Å in **2**.

Keywords: silver complex, coordination chemistry, crystal structure, self-assembly, hydrogen bonding.

INTRODUCTION

There have recently been great advances in the synthesis of complex structures, including polymers, two-dimensional sheet structures, helices, and cage complexes, through the use of dynamic coordination chemistry [1—3]. Silver(I) is particularly useful in the self-assembly of complex structures since it is a labile metal center with versatile coordination properties [4—6]. Silver(I) complexes with carboxylates and organic amines are a group of metal complexes that because of their versatile structures and wide usage in many fields have attracted much attention in recent years [7—9]. Studying the variety of products in the self-assembly processes between labile metal ions and multidentate ligands is an interesting topic in supramolecular chemistry. In this paper, the synthesis and structures of two new dinuclear silver(I) complexes $[\text{Ag}_2(\text{DAP})_2](\text{BPC}) \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ag}_2(\text{BPC})(\text{AMP})_4] \cdot 2\text{H}_2\text{O}$ (**2**), where DAP, BPC, and AMP are 1,3-diaminopropane, 4,4'-biphenyldicarboxylate, and 2-amino-5-methylpyridine respectively, have been synthesized and structurally characterized.

EXPERIMENTAL

Materials and methods. All chemicals were available commercially as analytical grade from Aldrich and were used without further purification. The C, H and N microanalyses were carried out using a Perkin-Elmer 240Q elemental analyzer.

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Synthesis of $[\text{Ag}_2(\text{DAP})_2](\text{BPC}) \cdot 2\text{H}_2\text{O}$ (1**).** 4,4'-Biphenyldicarboxylic acid (1.0 mmol, 242.0 mg) and Ag_2O (0.5 mmol, 115.8 mg) were dissolved in a 30 % aqueous ammonia solution (70 ml), and the mixture was stirred for about 2 h until the solid disappeared. To the solution was added with stirring a methanol solution (10 ml) of 1,3-diaminopropane (2.0 mmol, 148.0 mg). The mixture was further stirred at room temperature at dark for 2 h, and the resulting colorless solution was kept in the dark for 5 days. Colorless block-shaped crystals of complex **1** were formed by the slow evaporation of the solvent. Yield: 53 %. Anal. Calcd. (%) for $\text{C}_{20}\text{H}_{36}\text{Ag}_2\text{N}_4\text{O}_8$: C, 35.5; H, 5.4; N, 8.3. Found (%): C, 35.2; H, 5.6; N, 8.5.

Synthesis of $[\text{Ag}_2(\text{BPC})(\text{AMP})_4] \cdot 2\text{H}_2\text{O}$ (2**).** 4,4'-Biphenyldicarboxylic acid (1.0 mmol, 242.0 mg) and Ag_2O (0.5 mmol, 115.8 mg) were dissolved in a 30 % aqueous ammonia solution (70 ml), and the mixture was stirred for about 2 h until the solid disappeared. To the solution was added with stirring a methanol solution (10 ml) of 2-amino-5-methylpyridine (2.0 mmol, 216.0 mg). The mixture was further stirred at room temperature at dark for 2 h, and the resulting colorless solution was kept in the dark for 7 days. Colorless block-shaped crystals of complex **2** were formed by the slow evaporation of the solvent. Yield: 62 %. Anal. Calcd. (%) for $\text{C}_{38}\text{H}_{44}\text{Ag}_2\text{N}_8\text{O}_6$: C, 49.4; H, 4.8; N, 12.1. Found (%): C, 49.8; H, 5.1; N, 11.8.

Caution! Silver carboxylates are potentially explosive. Only small quantities of material should be prepared and handled with great care.

X-ray crystallography. Suitable single crystals of the complexes were selected and mounted on glass fibers for data collection performed on a Bruker SMART 1000 CCD area diffractometer equipped with a graphite-monochromatic MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. The unit cell dimensions were obtained with the least-squares refinements and the structures were solved by direct methods using the SHELXTL-97 program [10]. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms on F^2 . Water H atoms in both complexes and the amino H atoms in **2** were located from difference Fourier maps and refined isotropically, with O—H, N—H, and H \cdots H distances restrained to 0.85(1) \AA , 0.90(1) \AA , and 1.45(2) \AA respectively. Other hydrogen atoms in the complexes were placed in calculated positions and constrained to ride on their parent atoms. The multi-scan absorption correction was applied by using the SADABS program [11]. The crystallographic data and experimental details for the structural analysis of the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonds are listed in Table 3. The atomic coordinates and isotropic thermal parameters are given in Table 4. CCDC-772559 for **1** and 772558 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: data_request@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

Both complexes were prepared according to the similar procedure. The mere difference is the N-containing ligands *viz.* flexible 1,3-diaminopropane for **1** and rigid 2-amino-5-methylpyridine for **2**. The crystals of the complexes must be kept in dark or they are readily decomposed.

$[\text{Ag}_2(\text{DAP})_2](\text{BPC}) \cdot 2\text{H}_2\text{O}$ (1**).** The molecular structure of complex **1** is shown in Fig. 1. The complex consists of a 12-membered macrocyclic dinuclear silver(I) dicationic ring, a 4,4'-biphenyldicarboxylate anion, and two water molecules of crystallization. The Ag \cdots Ag separation is 5.127(2) \AA . Each Ag atom is coordinated by two N atoms from two DAP ligands, forming a distorted linear geometry. The N1—Ag1—N2A bond angle is 174.2(1) $^\circ$, which deviates from the ideal value of 180 $^\circ$ for the linear geometry by 5.8(1) $^\circ$. The Ag—N bond lengths are comparable to those observed in other silver(I) complexes with organic amines [12–14]. BPC acts as a counterion and does not coordinate to the silver atoms. The dihedral angle between the C4—C9 benzene ring and the O1—C10—O2 plane is 4.5(2) $^\circ$.

Table 1

Crystal Data and Structure Refinement for the Complexes

| | 1 | 2 |
|---|---|---|
| Empirical formula | C ₂₀ H ₃₆ Ag ₂ N ₄ O ₈ | C ₃₈ H ₄₄ Ag ₂ N ₈ O ₆ |
| Formula weight | 676.3 | 924.6 |
| Temperature, K | 298(2) | 298(2) |
| Wavelength, Å | 0.71073 | 0.71073 |
| Crystal shape/colour | Block/colorless | Block/colorless |
| Crystal size, mm | 0.38 × 0.32 × 0.27 | 0.30 × 0.27 × 0.23 |
| Crystal system | Triclinic | Triclinic |
| Space group | <i>P</i> -1 | <i>P</i> -1 |
| <i>a</i> , <i>b</i> , <i>c</i> , Å | 8.585(2), 8.849(2), 9.890(3) | 11.818(3), 13.132(4), 13.281(4) |
| α , β , γ , deg. | 107.893(3), 94.139(3), 113.202(3) | 92.571(4), 96.425(3), 102.142(4) |
| <i>V</i> , Å ³ | 640.9(3) | 1997.5(10) |
| <i>Z</i> | 1 | 2 |
| <i>D</i> _c , g/cm ³ | 1.752 | 1.537 |
| Absorption coefficient, mm ⁻¹ | 1.578 | 1.035 |
| <i>F</i> (000) | 342 | 940 |
| θ range, deg. | 2.22 / 27.49 | 2.21 / 27.50 |
| Index ranges (<i>h</i> , <i>k</i> , <i>l</i>) | -9/11, -11/6, -12/12 | -15/12, -14/17, -17/17 |
| <i>R</i> _{int} | 0.0213 | 0.0197 |
| Reflections collected | 3872 | 12076 |
| Independent reflections | 2837 | 8824 |
| Observed reflections with <i>I</i> > 2 σ (<i>I</i>) | 2599 | 6539 |
| Min. and max. transmission | 0.585/0.675 | 0.746/0.797 |
| Goodness-of-fit on <i>F</i> ² | 1.049 | 1.027 |
| <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^a | 0.0285, 0.0729 | 0.0382, 0.0783 |
| <i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a | 0.0314, 0.0752 | 0.0575, 0.0873 |
| Large diff. peak and hole, e/Å ³ | 0.457 and -0.474 | 0.459 and -0.780 |

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

Table 2

Selected Bond Distances and Angles

| 1 | | | | 2 | | | |
|--------------|----------|--------------|-----------|--------------|----------|--------------|------------|
| Distances, Å | | Angles, deg. | | Distances, Å | | Angles, deg. | |
| Ag1—N1 | 2.154(2) | N2A—Ag1—N1 | 174.21(8) | Ag1—N3 | 2.178(2) | N7—Ag1—N3 | 154.50(10) |
| Ag1—N2A | 2.142(2) | | | Ag1—O2 | 2.410(2) | N3—Ag1—O2 | 98.92(9) |
| | | | | Ag2—N5 | 2.176(2) | N1—Ag2—O1 | 106.89(9) |
| | | | | Ag1—N7 | 2.177(3) | N7—Ag1—O2 | 106.52(10) |
| | | | | Ag2—N1 | 2.160(2) | N1—Ag2—N5 | 158.55(9) |
| | | | | Ag2—O1 | 2.514(2) | N5—Ag2—O1 | 93.99(9) |

Symmetry code: A) 1-x, 1-y, -z.

Table 3

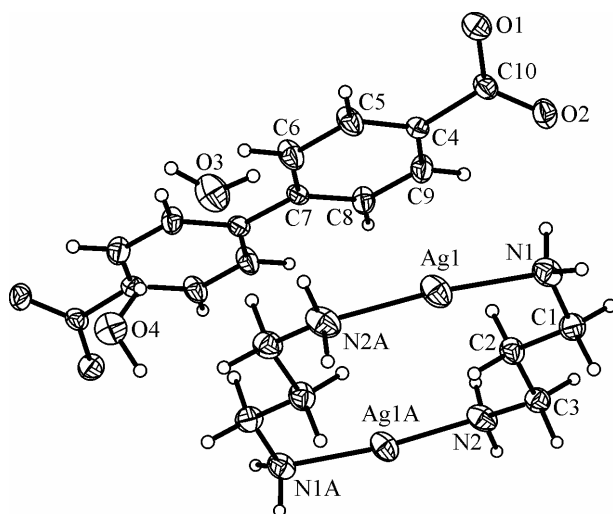
Hydrogen Geometries

| D—H···A | $d(\text{D—H}), \text{\AA}$ | $d(\text{H}\cdots\text{A}), \text{\AA}$ | $d(\text{D}\cdots\text{A}), \text{\AA}$ | Angle (D—H···A), deg. |
|---------------------------|-----------------------------|---|---|-----------------------|
| 1 | | | | |
| O4—H4A···O3 | 0.843(10) | 2.02(2) | 2.807(3) | 154(4) |
| O3—H3D···O2 ^{#1} | 0.854(10) | 1.904(13) | 2.747(3) | 169(4) |
| O4—H4B···O1 ^{#2} | 0.848(10) | 1.932(16) | 2.748(3) | 161(3) |
| N2—H2B···O1 ^{#1} | 0.90 | 2.50 | 3.216(3) | 137 |
| N2—H2A···O3 ^{#3} | 0.90 | 2.32 | 3.192(4) | 162 |
| N1—H1B···O4 ^{#4} | 0.90 | 2.25 | 3.145(3) | 172 |
| N1—H1A···O2 | 0.90 | 2.14 | 3.001(3) | 160 |
| 2 | | | | |
| O6—H6D···O2 ^{#5} | 0.847(10) | 2.53(4) | 2.917(4) | 109(3) |
| O5—H5A···O4 ^{#6} | 0.849(10) | 2.032(18) | 2.848(4) | 161(4) |
| O5—H5B···O4 ^{#2} | 0.851(10) | 2.006(13) | 2.848(4) | 170(4) |
| N8—H8A···O2 | 0.894(10) | 2.127(14) | 2.994(4) | 163(3) |
| N4—H4A···O3 ^{#7} | 0.892(10) | 1.874(11) | 2.763(4) | 175(4) |
| N2—H2B···O1 | 0.890(10) | 2.127(12) | 3.005(4) | 168(3) |
| N8—H8B···O6 ^{#8} | 0.891(10) | 2.017(12) | 2.898(5) | 169(3) |
| N6—H6B···O5 ^{#8} | 0.892(10) | 2.183(16) | 3.045(4) | 162(3) |
| N2—H2A···O5 | 0.891(10) | 2.114(13) | 2.990(4) | 167(4) |

Symmetry codes: #1: $1-x, 2-y, 1-z$; #2: $1-x, 1-y, 1-z$; #3: $1-x, 1-y, -z$; #4: $1+x, 1+y, z$; #5: $1-x, -y, 1-z$; #6: $x, y, -1+z$; #7: $1+x, y, -1+z$; #8: $1+x, y, z$.

In the crystal structure of **1**, the 12-membered macrocyclic dinuclear silver(I) dicationic rings and the 4,4'-biphenyldicarboxylates are linked through intermolecular N—H···O hydrogen bonds, forming layers parallel to the *ab* plane. The layers are further linked with water molecules through intermolecular N—H···O and O—H···O hydrogen bonds to form a three-dimensional network, as shown in Fig. 2.

[Ag₂(BPC)(AMP)₄·2H₂O (**2**). The molecular structure of complex **2** is shown in Fig. 3. The



complex consists of a dinuclear silver(I) complex molecule and two water molecules of crystallization. Each Ag atom is three-coordinated by two pyridine N atoms from two AMP ligands and one carboxylate O atom of a BPC ligand, forming a distorted T-shaped geometry. The two adjacent Ag atoms are bridged by a carboxylate group, with the Ag···Ag separation being 3.172(2) Å, which is comparable with the Ag···Ag separations in other carboxylatebridged

Fig. 1. View of the molecular structure of complex (1) with 30% thermal ellipsoids. Atoms labeled with the suffix A or unlabeled are at the symmetry position $1-x, 1-y, -z$

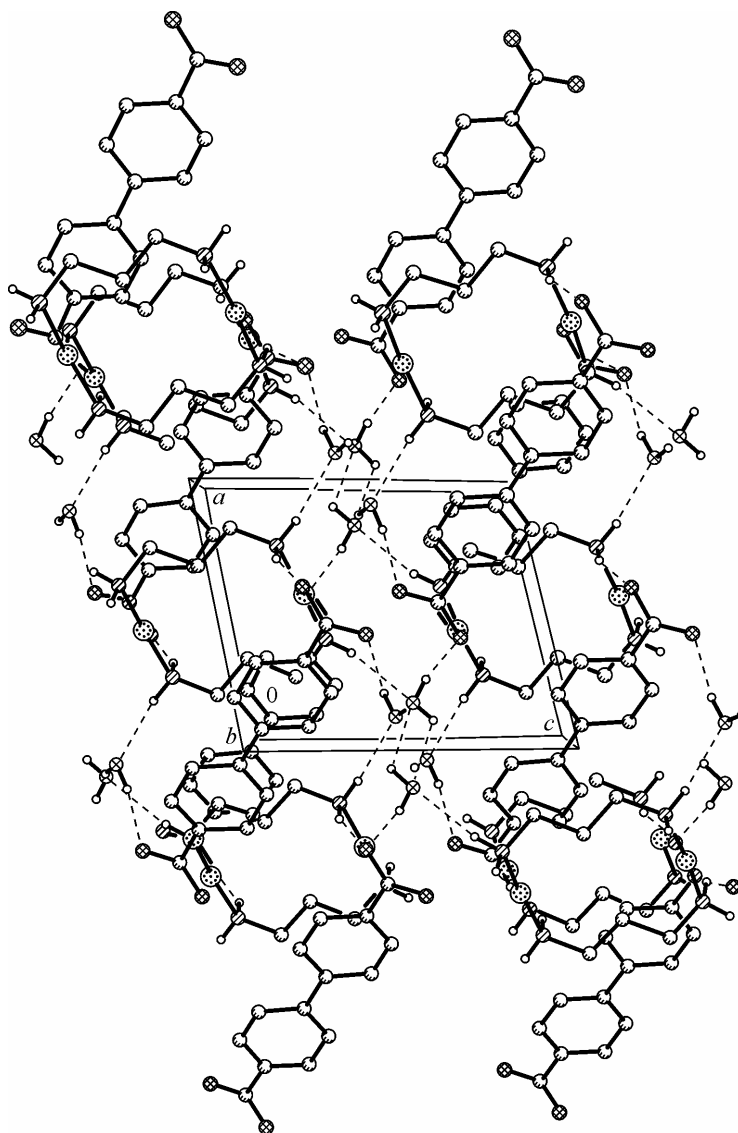


Fig. 2. Molecular packing of complex **1** viewed along the *b* axis. Hydrogen bonds are shown as dashed lines

silver(I) complexes [15, 16]. The N3—Ag1—N7 and N1—Ag2—N5 bond angles are $154.5(1)^\circ$ and $158.6(1)^\circ$ respectively, which deviate from the ideal value of 180° for the perfect T-shaped geometry. The O2—Ag1—N3, O2—Ag1—N7, O1—Ag2—N1, and O1—Ag2—N5 bond angles also deviate from the ideal value of 90° for a perfect T-shaped geometry, ranging from $94.0(1)^\circ$ to $106.9(1)^\circ$. The Ag—N bond lengths are comparable to those in **1** and also comparable to those observed in other silver(I) complexes with pyridine derivatives [17—19]. The Ag—O bond lengths are comparable to those observed in other silver(I) complexes with carboxylate bridges [15, 16]. The dihedral angle between the C1—C6 benzene ring and the O1—C13—O2 plane is $10.0(2)^\circ$, and that between the C7—C12 benzene ring and the O3—C14—O4 plane is $34.8(2)^\circ$. The dihedral angle between the two benzene rings is $31.9(2)^\circ$.

Molecular packing of the complex is shown in Fig. 4. The dinuclear complex molecules are linked through intermolecular N—H \cdots O hydrogen bonds, forming layers parallel to the *ac* plane. The layers are further linked with water molecules through intermolecular N—H \cdots O and O—H \cdots O hydrogen bonds to form a three-dimensional network. In addition, there are $\pi\cdots\pi$ stacking interactions among the adjacent benzene and pyridine rings (Table 4) [20].

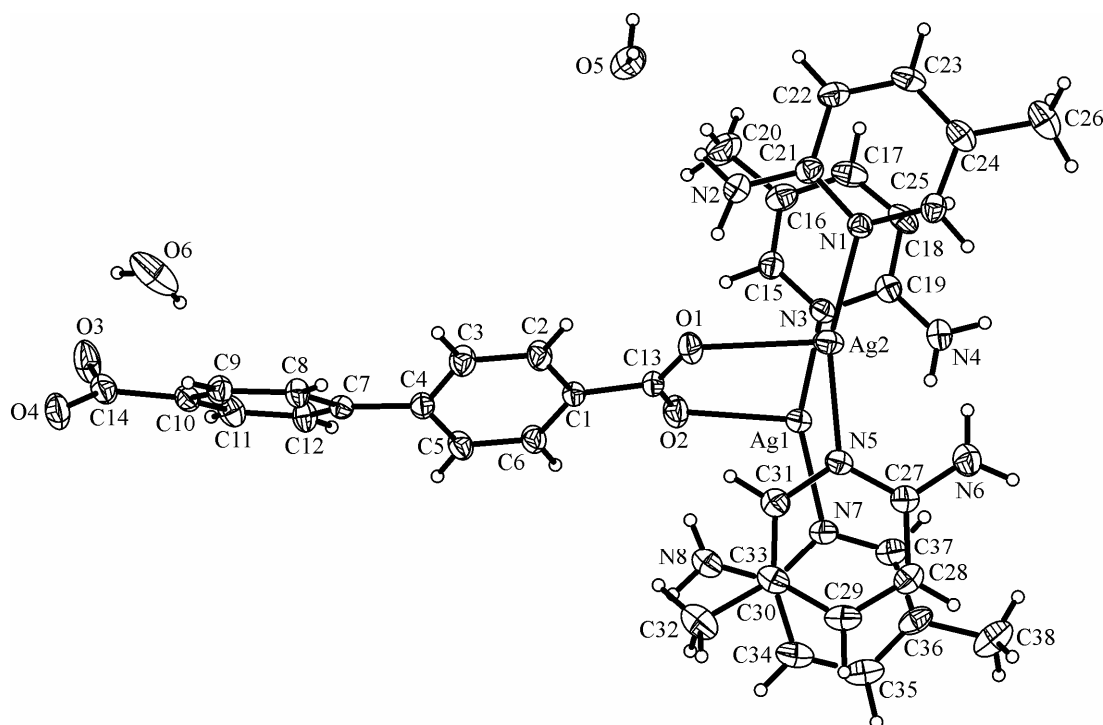
Fig. 3. View of the molecular structure of complex **2** with 30 % thermal ellipsoids

Table 4

Parameters between the Planes

| Cg | Distance between ring centroids, Å | Dihedral angle, deg. | Perpendicular distance of Cg(I) on Cg(J), Å | Perpendicular distance of Cg(J) on Cg(I), Å |
|----------------------------|------------------------------------|----------------------|---|---|
| Cg(1)—Cg(1) ^{#9} | 3.697 | 0.03 | 3.268 | 3.268 |
| Cg(1)—Cg(2) | 3.588 | 10.32 | 3.335 | 3.225 |
| Cg(2)—Cg(2) ^{#10} | 4.237 | 0.02 | 3.313 | 3.313 |
| Cg(2)—Cg(4) ^{#10} | 5.414 | 8.11 | 2.930 | 2.809 |
| Cg(3)—Cg(1) ^{#9} | 5.874 | 11.44 | 2.653 | 3.436 |
| Cg(3)—Cg(4) | 3.516 | 5.63 | 3.331 | 3.344 |
| Cg(3)—Cg(5) ^{#11} | 5.630 | 58.23 | 2.103 | 4.776 |
| Cg(3)—Cg(6) ^{#11} | 4.842 | 88.60 | 0.112 | 4.656 |
| Cg(4)—Cg(2) ^{#10} | 5.414 | 8.11 | 2.809 | 2.930 |
| Cg(4)—Cg(3) | 3.516 | 5.63 | 3.344 | 3.331 |
| Cg(4)—Cg(5) ^{#12} | 5.082 | 56.02 | 1.740 | 4.482 |
| Cg(4)—Cg(6) ^{#12} | 5.608 | 85.38 | 0.767 | 4.963 |
| Cg(5)—Cg(1) ^{#13} | 5.692 | 51.07 | 2.400 | 4.311 |
| Cg(5)—Cg(4) ^{#14} | 5.170 | 56.02 | 1.973 | 4.854 |
| Cg(6)—Cg(1) ^{#13} | 4.945 | 79.61 | 1.715 | 4.561 |
| Cg(6)—Cg(3) ^{#14} | 5.575 | 88.60 | 1.280 | 5.252 |
| Cg(6)—Cg(4) ^{#14} | 5.226 | 85.38 | 2.454 | 4.465 |

Symmetry codes: #9: $2-x, 1-y, -z$; #10: $2-x, -y, -z$; #11: $2-x, 1-y, 1-z$; #12: $2-x, -y, 1-z$; #13: $x, y, 1+z$; #14: $-1+x, y, z$. Cg(1), Cg(2), Cg(3), Cg(4), Cg(5), and Cg(6) are the centroids of N1—C21—C22—C23—C24—C25, N3—C15—C16—C17—C18—C19, N5—C27—C28—C29—C30—C31, N7—C33—C34—C35—C36—C37, C1—C2—C3—C4—C5—C6, and C7—C8—C9—C10—C11—C12, respectively.

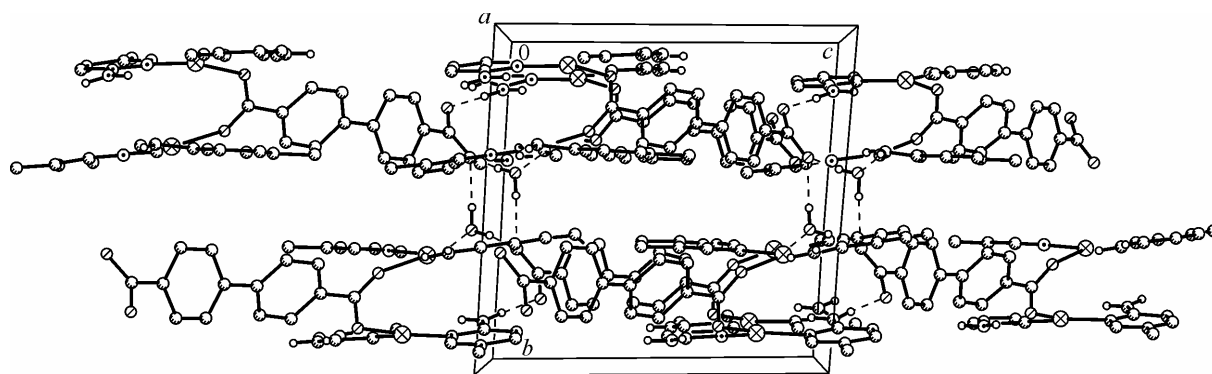


Fig. 4. Molecular packing of complex 2 viewed along the *a* axis. Hydrogen bonds are shown as dashed lines

CONCLUSIONS

Two new dinuclear silver(I) complexes have been prepared and characterized by X-ray crystallography. The N atoms of 1,3-diaminopropane and the pyridine N atom of 2-amino-5-methylpyridine easily coordinate to the Ag atoms, while the amino N atom of 2-amino-5-methylpyridine does not participate in the coordination. The carboxylate group of 4,4'-biphenyldicarboxylate can participate in the coordination only when there is a suitable separation between the two adjacent Ag atoms.

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