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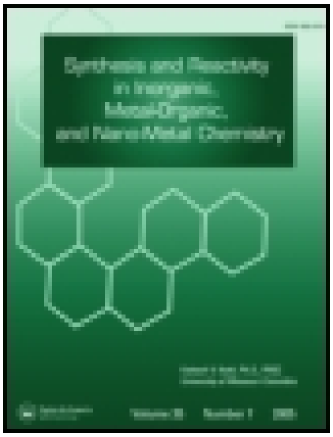

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Synthesis and Crystal Structures of Two Silver(I) Complexes Derived from 2-Amino-4-methylpyridine with 2-Aminobenzoic Acid and Nicotinic Acid

Feng-Wu Wang [a] , Yi-Jun Wei [a] & Qi-Yong Zhu [a]
[a] Department of Chemistry , Huainan Normal College , Huainan, P. R. China

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Synthesis and Crystal Structures of Two Silver(I) Complexes Derived from 2-Amino-4-methylpyridine with 2-Aminobenzoic Acid and Nicotinic Acid

Feng-Wu Wang, Yi-Jun Wei, and Qi-Yong Zhu
Department of Chemistry, Huainan Normal College, Huainan, P. R. China

The reaction of Ag_2O and 2-amino-4-methylpyridine (AMP) with 2-aminobenzoic acid (HAC) and nicotinic acid (HNA), respectively, afforded two silver(I) complexes, $[Ag(AMP)_2]{\cdot}AC$ (1) and $[Ag(AMP)(NA)]_n{\cdot}nH_2O$ (2). Both complexes were characterized by elemental analyses and X-ray single-crystal diffraction. Complex (1) is a mononuclear silver(I) complex, in which the Ag atom is in a linear geometry, while complex (2) is a pyridine-3-carboxylate bridged polynuclear silver(I) complex, in which the Ag atom is in a distorted triangular geometry. Both crystals are stabilized by intermolecular hydrogen bonds.

Keywords crystal structure, hydrogen bonding, silver, synthesis

INTRODUCTION

In the last few years, there have been major advances in the synthesis of complex structures, including polymers, two-dimensional sheets, helices, and cages, through the use of dynamic coordination chemistry.[1–6] Among the metal ions, silver is of particular interest in the self-assembly of complex structures since it is a labile metal center with versatile coordination modes.[7–9] 2-aminobenzoic acid (HAC) and nicotinic acid (HNA) are two versatile ligands in the synthesis of silver(I) complexes, which readily adopt bridging modes.[10,11] 2-amino-4-methylpyridine (AMP) is also a useful ligand in the synthesis of silver(I) complexes.[12,13] In order to investigate the aggregates of such components, in this paper, two silver(I) complexes have been synthesized and structurally characterized.

EXPERIMENTAL

Materials and Measurements

All the starting materials for synthesis were of analytical grade as purchased from Aldrich and were used without further purification. Elemental analyses were carried out on a Perkin-Elmer model 240 analyzer.

Synthesis of $[Ag(AMP)_2]{\cdot}AC$ (1)

Ag_2O (0.1 mmol, 23.2 mg) and HAC (0.2 mmol, 27.5 mg) were dissolved in a 30% ammonia solution (10 ml) and stirred for 30 min to give a clear colorless solution. To the above solution was added with stirring a methanol solution (3 mL) of AMP (0.2 mmol, 21.6 mg). The mixture was stirred for another 30 min, and the resulting clear solution was kept in dark at room temperature for a week. Colorless block-shaped crystals of (**1**) were formed. The crystals were isolated by filtration. Yield: 31% on the basis of Ag_2O. Anal. calcd. for $C_{19}H_{22}AgN_5O_2$(FW 460.3): C, 49.6; H, 4.8; N, 15.2. Found: C, 49.1; H, 5.0; N, 15.5%.

Synthesis of $[Ag(AMP)(NA)]_n{\cdot}nH_2O$ (2)

Complex (**2**) was synthesized by a similar method as that described for (**1**), with HAC replaced by HNA (0.2 mmol, 24.5 mg), yielding colorless block-shaped crystals. Yield: 45% on the basis of Ag_2O. Anal. calcd. for $C_{12}H_{14}AgN_3O_3$ (FW 356.1): C, 40.5; H, 4.0; N, 11.8. Found: C, 41.0; H, 4.1; N, 11.5%.

Crystal Structure Determination

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART APEX 1000 area-detector with Mo*Ka* radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program,[14] and multi-scan absorption corrections were performed using the SADABS program.[15] The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL program.[16] Non-hydrogen atoms were refined with anisotropic displacement parameters. The amino H atoms in both complexes and the water H atoms in (**2**) were located in difference Fourier maps and refined isotropically, with N–H and O–H distances

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Address correspondence to Yi-Jun Wei, Department of Chemistry, Huainan, 232001, China. E-mail: huainanweiyijun@163.com

TABLE 1
Crystallographic and experimental data for complexes (**1**) and (**2**)

Complexes	(**1**)	(**2**)
Formula	$C_{19}H_{22}AgN_5O_2$	$C_{12}H_{14}AgN_3O_3$
FW	460.3	356.1
Crystal shape/color	block/colorless	block/colorless
Crystal size/mm	0.20×0.18×0.17	0.43×0.40×0.38
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	Cc
a/Å	16.229(1)	10.756(2)
b/Å	7.070(1)	8.718(2)
c/Å	17.979(1)	14.599(3)
β/°	112.412(2)	107.711(3)
V/Å^3	1907.1(3)	1304.1(5)
Z	4	4
T/K	298(2)	298(2)
μ/mm^{-1}(Mo-Kα)	1.081	1.553
D_c/g cm^{-3}	1.603	1.814
Reflections/parameters	4125/330	2139/629
Independent reflections	3497	2086
$F(000)$	936	712
$T_{\min}$	0.813	0.555
$T_{\max}$	0.837	0.590
Goodness of fit on F^2	1.059	1.057
R_1, wR_2 $[I \geq 2\sigma(I)]^{a)}$	0.0278, 0.0721	0.0503, 0.0203
R_1, wR_2 (all data)$^{a)}$	0.0346, 0.0762	0.0507, 0.0210

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

restrained to 0.90(1) and 0.85(1) Å, respectively. All other hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. The coordinate bond lengths and angles are listed in Table 2. Hydrogen bonds are listed in Table 3.

TABLE 2
Selected bond lengths (Å) and angles (°) for the complexes (**1**) and (**2**)

	(1)		
Ag1—N1	2.1080(18)	Ag1—N3	2.1077(18)
N3—Ag1—N1	177.66(7)		
	(2)		
Ag1—N1	2.206(2)	Ag1—N3	2.259(2)
Ag1—O1A	2.447(2)		
N1—Ag1—N3	131.90(10)	N1—Ag1—O1A	130.78(9)
N3—Ag1—O1A	95.30(9)		

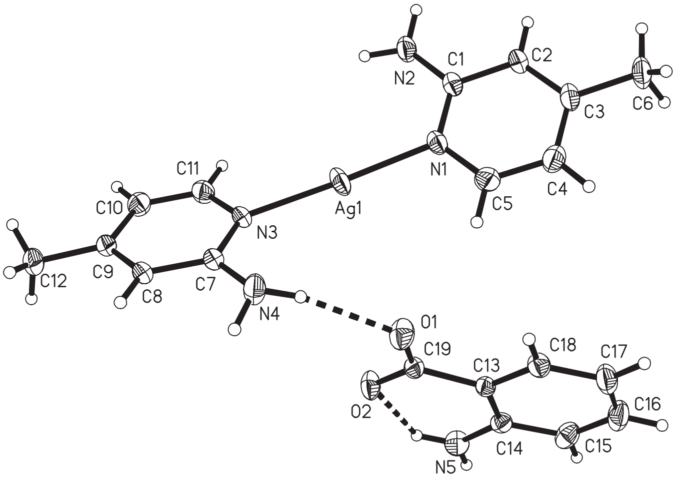

FIG. 1. Molecular structure of (**1**) with 30% probability thermal ellipsoids. H atoms not related to the hydrogen bonding are omitted. Hydrogen bond as dashed lines. Atoms with the suffixes A and B are at the positions $1 + x, y, z$ and $-x, 1 - y, -z$, respectively.

RESULTS AND DISCUSSION

Preparation of the Complexes

The reaction of Ag_2O with HAC and HNA, respectively, forms the corresponding silver(I) carboxylates.[10,17,18] The silver(I) carboxylates are readily react with organic compounds containing N atoms, forming versatile structures.[19,20] In this paper, the AMP was added to the silver(I) carboxylates, yielding two polynuclear silver(I) complexes. The elemental analyses confirm the formulae of the complexes. The crystals of both complexes are stable in dark, soluble in 30% ammonia solution and acetonitrile.

Structure Description of the Two Complexes

The molecular structure of (**1**) is shown in Figure 1. The complex consists of a mononuclear silver(I) complex cation and a 2-aminobenzoate anion. An intramolecular N4—H4B···O1 hydrogen bond is observed between the two moieties. The Ag atom in the cation is coordinated by two N atoms from two AMP ligands, forming a linear geometry, with the N1-Ag1-N3 bond angle of 177.7(1)°. The coordinate bond lengths are comparable with the values observed in other similar silver(I) complexes.[11,21] The dihedral angle between the two pyridine rings is 28.2(3)°.

In the crystal structure of the complex, the AC anions are linked to the silver(I) cations through N—H···O hydrogen bonds. The aggregates are further linked through N—H···O hydrogen bonds, forming layers parallel to the *bc* plane, as shown in Figure 2.

The molecular structure of (**2**) is shown in Figure 3. The smallest repeat unit of the complex consists of an Ag atom, an AC ligand, an AMP ligand, and a water molecule of crystallization. The water molecule is linked to the silver(I)

TABLE 3
Hydrogen bond distances (Å) and angles (°) for the complexes (**1**) and (**2**)

D—H···*A*	*d*(*D*—H)	*d*(H···*A*)	*d*(*D*···*A*)	*Angle* (*D*—H···*A*)
(**1**)				
N4—H4A···O2^{i}	0.897(10)	2.39(3)	3.267(3)	168(3)
N2—H2B···O1^{ii}	0.897(10)	2.288(11)	3.166(3)	166(3)
N2—H2A···O2^{iii}	0.893(10)	1.996(12)	2.874(2)	167(3)
N5—H5B···O1^{iv}	0.879(10)	2.087(15)	2.924(3)	159(3)
N5—H5A···O2	0.88(2)	2.00(2)	2.656(3)	131(2)
N4—H4B···O1	0.898(10)	2.10(3)	2.988(3)	169(3)
(**2**)				
O3—H3B···O1	0.85(3)	1.95(3)	2.787(4)	169(4)
N2—H2A···O2^{v}	0.89(4)	2.15(4)	3.025(4)	171(5)
N2—H2B···O3^{vi}	0.89(3)	2.07(4)	2.923(4)	161(4)
O3—H3A···O2^{vii}	0.86(4)	1.98(4)	2.811(4)	165(5)

Symmetry codes for i) $-x$, $1-y$, $1-z$; ii) x, $3/2-y$, $-1/2+z$; iii) $-x$, $1/2+y$, $1/2-z$; iv) x, $-1+y$, z; v) $-x$, $1-y$, $1-z$.

complex molecule through intramolecular O3—H3B···O1 hydrogen bond. The AMP ligands linked to the silver(I) moieties through the Ag-N(pyridine) coordination bonds. The HAC ligand acts as a bridging group, which coordinates to two Ag atoms through the pyridine N atom and one phenolate O atom.

Each Ag atom in the complex is three-coordinated in a distorted triangular geometry, with one N and one O atoms from two AC ligands, and with one pyridine N atom of one AMP ligand. The triangular geometry of the coordination is distorted, as evidenced by the coordinate bond angles. The bond angles of N1-Ag1-N3 and N1-Ag1-O1A are 131.9(1) and 130.8(1)°, respectively, which deviates from the ideal value of 120° for a perfect triangular geometry. The N3-Ag1-O1A bond angle of 95.3(1)° is also deviates from the ideal value of 120° for a perfect triangular geometry. The coordinate bond lengths are comparable with those of (**1**), and also comparable with the values observed in other similar silver(I) complexes.[22,23]

In the crystal structure of the complex, the molecules are linked through intermolecular N—H···O and O—H···O hydrogen bonds, forming a three-dimensional network, as shown in Figure 4.

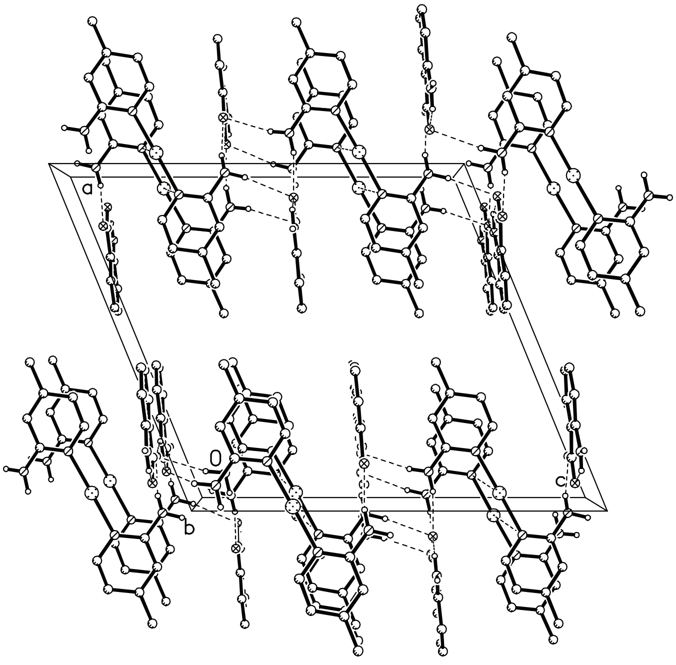

FIG. 2. Molecular packing of (**1**), viewed along the *b* axis.

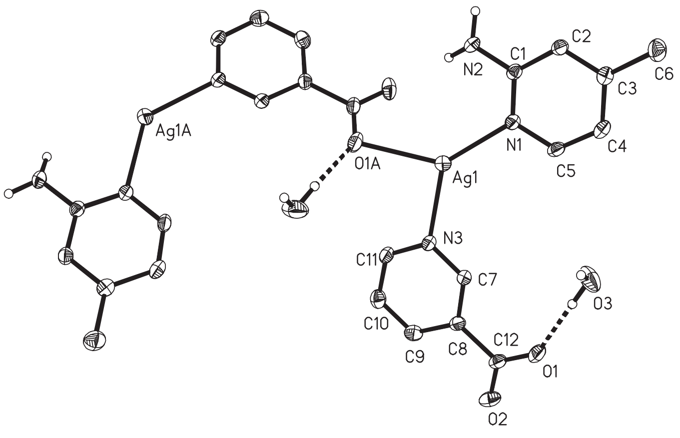

FIG. 3. Molecular structure of (**2**) with 30% probability thermal ellipsoids. H atoms not related to the hydrogen bonding are omitted. Hydrogen bond as dashed lines. Atoms with the suffixes A, B and C are at the positions $-x$, $1-y$, $1-z$; x, $3/2-y$, $-1/2+z$; and $-x$, $-1/2+y$, $3/2-z$, respectively.

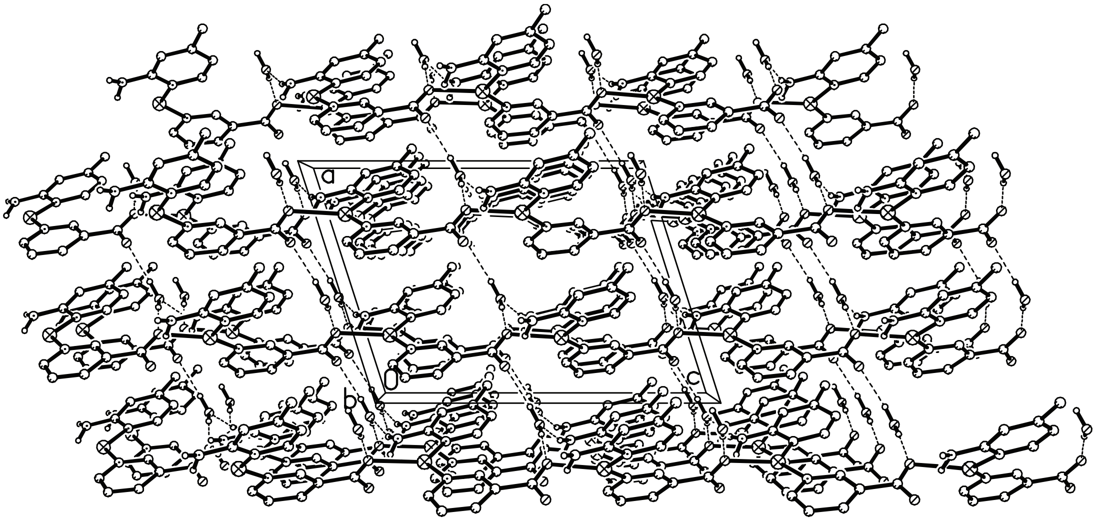

FIG. 4. Molecular packing of (**2**), viewed along the *a* axis.

CONCLUSION

A mononuclear silver(I) complex and a polynuclear silver(I) complex were synthesized and characterized by elemental analysis and X-ray single-crystal diffraction. The nicotinic acid is a versatile ligand in the synthesis of silver(I) complexes, which readily adopt bridging modes in the coordination. The coordination of the 2-aminobenzoic acid and 2-amino-4-methylpyridine indicates that the pyridine N atom readily coordinates to the Ag atom, while the amino N atom seldom coordinates to the Ag atom. Instead, the amino N atoms contribute to the formation of hydrogen bonds, and stabilize the crystal structures.

Supplementary Material

CCDC 741187 and 741188 contain the supplementary crystallographic data for (**1**) and (**2**), respectively. These data can be obtained free of charge *via* http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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