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Syntheses and Structural Characterization of Silver(I) Complexes with Pyridine and Carboxylate Derivatives[1]

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Abstract—Self-assembly between silver carboxylates with 2-aminopyridine derivatives give two silver(I) complexes, $[[Ag(5MP)_2(CNB)] \cdot NH_3$ (**I**) and $[Ag(3MP)_2(HMB)]$ (**II**), where 5MP, CNB, 3MP, and HMB represent 2-amin-5-methylpyridine, 5-chloro-2-nitrobenzoate, 2-amino-3-methylpyridine, and 2-hydroxy-3-methoxybenzoate, respectively. The crystal structures of the complexes were investigated. The Ag atom in each complex is coordinated by two pyridine N atoms and weakly coordinated by a carboxylic O atom. The crystal of **I** is triclinic: space group $P\overline{1}$, $a = 7.562(2)$, $b = 11.708(3)$, $c = 12.933(3)$ Å, $\alpha = 103.378(4)°$, $\beta = 93.910(4)°$, $\gamma = 99.001(4)°$, $V = 1093.7(5)$ Å^3, $Z = 2$. The crystal of **II** is monoclinic: space group $C2/c$, $a = 25.727(5)$, $b = 10.274(2)$, $c = 19.872(4)$ Å, $\beta = 126.62(3)°$, $V = 4215.7(15)$ Å^3, $Z = 4$.

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INTRODUCTION

Silver(I) carboxylates with organic amines form an important class of metal complexes in coordination chemistry. These complexes have been received much attention in many fields, and their crystal structures have widely been investigated [1–5]. Studying the variety of products in the self-assembly processes between the silver atoms with nitrogen- and oxygen-containing ligands is an interesting topic in supramolecular chemistry. The balance between the formation of different structures is often subtle. Factors that affect the coordination topology include not only the highly influential factors of metal and ligand coordination preferences but also anion-based influences. The latter factor is particularly notable in the silver complexes [6, 7]. In the present work, two silver(I) complexes, $[Ag(5MP)_2(CNB)] \cdot NH_3$ (**I**) and $[Ag(3MP)_2(HMB)]$ (**II**), where 5MP, CNB, 3MP, and HMB represent 2-amino-5-methylpyridine, 5-chloro-2-nitrobenzoate, 2-amino-3-methylpyridine, and 2-hydroxy-3-methoxybenzoate, respectively, were synthesized and characterized by elemental analyses and single-crystal X-ray diffraction.

EXPERIMENTAL

Materials and instruments. The chemicals with AR grade were used as purchased from Aldrich without further purification. The silver(I) carboxylates were prepared by the reaction of Ag_2O with carboxylic acids in 30% ammonia solutions. C, H, and N elemental analyses were preformed with a PerkinElmer elemental analyzer.

Synthesis of complex I. Ag_2O (0.5 mmol, 0.116 g) and CNB (1.0 mmol, 0.201 g) were dissolved in a 30% ammonia solution (50 ml) and stirred for 30 min in dark to give a colorless solution. Then 5MP (2.0 mmol, 0.216 g) was added to the solution with continuous stiring for 30 min in dark at room temperature. Colorless block-shaped crystals of **I** were formed by the slow evaporation of the solution in dark. The crystals were isolated by filtration, washed with water and methanol. The yield was 0.370 g (69%).

For $C_{19}H_{22}Cl\,N_6O_4Ag$

anal. calcd., %:	C, 42.1;	H, 4.1;	N, 15.5.
Found, %:	C, 42.5;	H, 4.2;	N, 15.3%.

Synthesis of complex II. Ag_2O (0.5 mmol, 0.116 g) and HMB (1.0 mmol, 0.168 g) were dissolved in a 30% ammonia solution (50 ml), and stirred for 30 min in dark to give a colorless solution. Then 3MP (2.0 mmol, 0.216 g) was added to the solution with continuous stiring for 30 min in dark at room temperature. Colorless block-shaped crystals of **II** were formed by the slow evaporation of the solution in dark. The crystals were isolated by filtration, and washed with water and methanol. The yield was 0.610 g (62%).

For $C_{40}H_{46}N_8O_8Ag_2$

anal. calcd., %:	C, 48.9;	H, 4.7;	N, 11.4.
Found, %:	C, 49.3;	H, 4.6;	N, 11.7.

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

Parameter	Value	
	I	**II**
Formula weight	541.75	982.59
Space group	Triclinic	Monoclinic
Unit cell dimensions:	$P\bar{1}$	$C2/c$
a, Å	7.562(2)	25.727(5)
b, Å	11.708(3)	10.274(2)
c, Å	12.933(3)	19.872(4)
α, deg	103.378(4)	90
β, deg	93.910(4)	126.62(3)
γ, deg	99.001(4)	90
V, Å^3	1093.7(5)	4215.7(15)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.645	1.548
μ, mm^{-1}	1.082	0.989
F(000)	548	2000
θ range, deg	1.63–27.00	1.97–27.50
Reflections measured	9244	17763
Independent reflections	4675	4803
Observed reflections	2359	2905
Variables	303	278
Restraints	12	6
R_1 ($I \geq 2\sigma(I)$)	0.0581	0.0658
wR_2 ($I \geq 2\sigma(I)$)	0.1352	0.1161
R_1 (all data)	0.1275	0.1193
wR_2 (all data)	0.1642	0.1335

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

Bond	d, Å	Bond	d, Å
I			
Ag(1)–N(1)	2.168(5)	Ag(1)–N(3)	2.181(5)
Ag(1)–O(1)	2.593(5)		
II			
Ag(1)–N(1)	2.151(4)	Ag(1)–N(3)	2.149(4)
Ag(1)–O(1)	2.747(4)	Ag(1)···Ag(1*A*)	3.131(2)
Angle	ω, deg	Angle	ω, deg
I			
N(1)Ag(1)N(3)	153.2(2)	N(1)Ag(1)O(1)	97.3(2)
N(3)Ag(1)O(1)	109.2(2)		
II			
N(1)Ag(1)N(3)	169.4(2)	N(1)Ag(1)O(1)	89.8(2)
N(3)Ag(1)O(1)	96.8(2)		

X-ray structure determination. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART APEX II area detector with MoK_α radiation (λ = 0.71073 Å). The collected data were reduced using the SAINT program [8], and multiscan absorption corrections were applied using the SADABS program [9]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL package [10]. All of the non-hydrogen atoms were refined anisotropically. Amino H atoms were located in difference Fourier maps and refined isotropically with N–H and H···H distances restrained to 0.90(1) and 1.43(2) Å. Other H atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Atomic coordinates and other structural parameters of the complexes have been deposited with the Cambridge Crystallographic Data Centre (nos. 769311 for **I** and 769312 for **II**; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The carboxylates CNB and HMB contain oxygen donors, which can react with Ag_2O to give silver(I) carboxylates. The pyridine derivatives 5MP and 3MP contain nitrogen donors. Since the silver atom has been classified as an extremely soft acid, it prefers to combine with the soft bases such as N-containing ligands [11, 12]. In the present work, the complexes were prepared by reaction of the silver(I) carboxylates with pyridine derivatives in 30% ammonia solutions. The pyridine N atoms are coordinate to the Ag atoms, however, the carboxylic O atoms are weakly coordinate to the Ag atoms.

The molecular structure of **I** is shown in Fig. 1. The complex consists of a mononuclear silver complex molecule and an ammonia molecule of crystallization. The Ag atom in the complex is coordinated by two pyridine N atoms from two 5MP ligands and by one carboxylic O atom of the CNB ligand. The amino N atoms of the 5MP ligands do not participate in the coordination. The O(1) atom of CNB is weakly coordinated to the Ag(1) atom with an Ag(1)–O(1) distance of 2.593(5) Å, which is longer than the normal Ag–O bonds [13, 14]. The Ag–N bonds in the com-

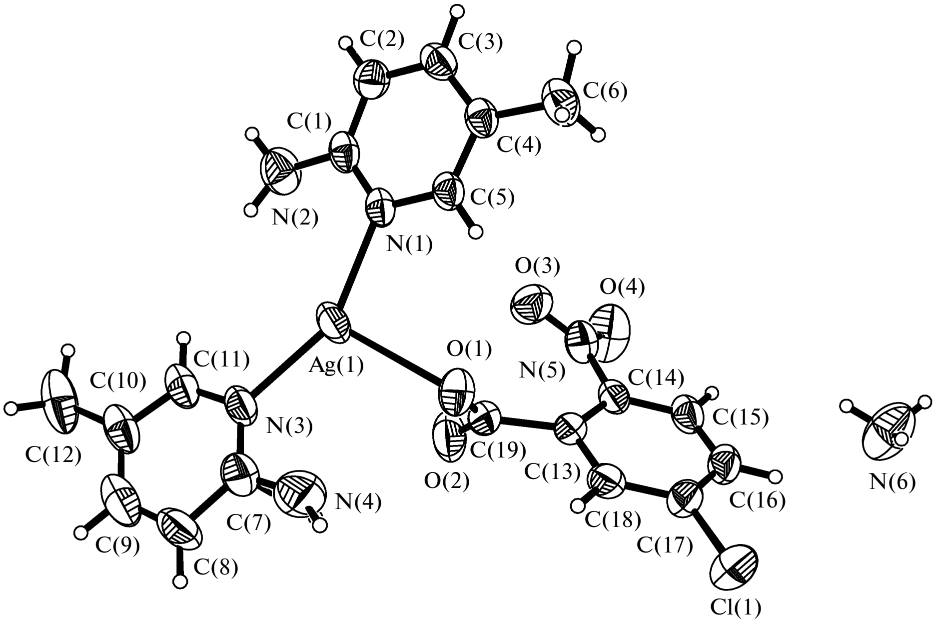

Fig. 1. Molecular structure of **I** showing 30% probability thermal ellipsoids.

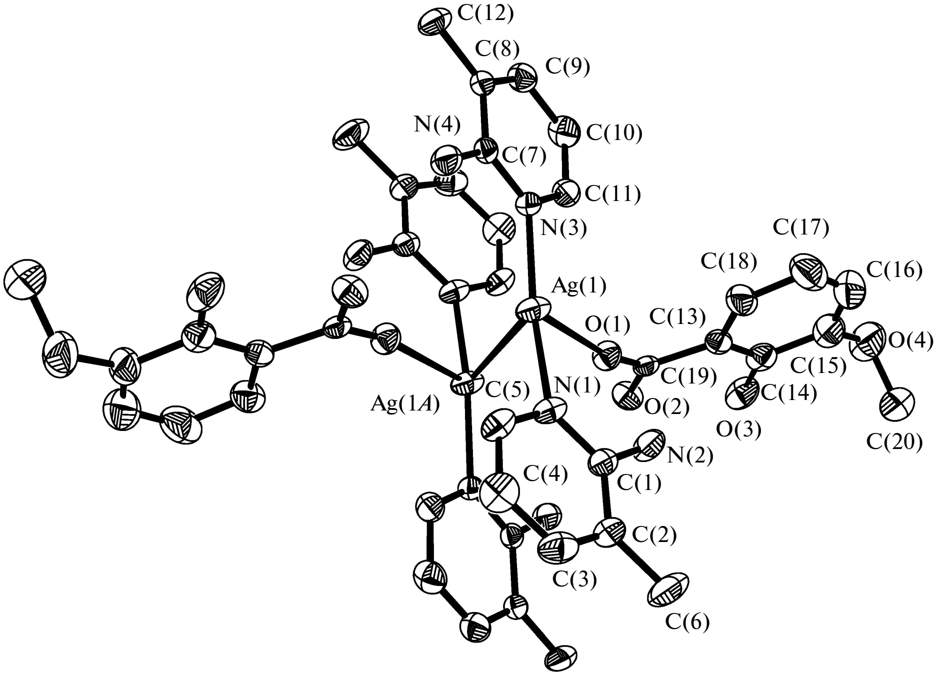

Fig. 2. Molecular structure of **II** showing 30% probability thermal ellipsoids; H atoms are omitted for clarity. Unlabelled atoms are at the symmetry position $-x$, $1 - y$, $-z$.

plex are typical and comparable with those observed in other silver complexes [15–17]. The C(13)–C(18) benzene ring forms dihedral angles of 57.4(6)° and 46.1(6)°, respectively, with the two pyridine rings.

The crystal structure of **II** is shown in Fig. 2. The compound is a mononuclear silver complex. The adjacent two mononuclear silver complex molecules are linked *via* Ag···Ag interactions (3.131(2) Å), forming a dimer. The Ag atom in the complex is coordinated by two pyridine N atoms from two 3MP ligands and by one carboxylic O atom of the HMB ligand. The amino N atoms of the 3MP ligands do not participate in the coordination. The O(1) atom of HMB is weakly coordinated to the Ag(1) atom with Ag–O distance of 2.747(4) Å, which is also longer than the normal Ag–O bonds [13, 14]. The Ag–N bonds in **II** are a little shorter than those in I, which might be caused by the weaker interaction of the Ag–O bond in **II** than that in **I**. The C(13)–C(18) benzene ring forms dihedral angles of 83.1(5)° and 75.1(5)°, respectively, with the two pyridine rings.

The stronger interaction between the Ag(1) and O(1) atoms in **I** than that in **II** can also be observed by the N(1)Ag(1)N(3) bond angles (153.2(2)° in **I**, 169.4(2)° in **II**).

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