

## A Novel Silver(I) $\sigma$ -Complex Supramolecular Polymer: [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub>

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The hydrothermal reactions of sodium *o*-hydroxybenzoate with AgNO<sub>3</sub> yield a novel stable Ag(I)  $\sigma$ -complex supramolecular polymer, [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub>. The structure of [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub> was solved by single crystal X-ray diffraction analysis. It is monoclinic with space group *P*2<sub>1</sub>/*c* and unit cell parameters *a*=0.7394(2) nm, *b*=0.8822(2) nm, *c*=1.0662(2) nm,  $\beta$ =107.66(3) $^\circ$ , *Z*=4. The silver(I) atom is two-coordinated by two carboxylic oxygen atoms of two *o*-hydroxybenzoate ligands, and meanwhile, forms supramolecular interaction with one carbon atom of phenyl-ring in the third *o*-hydroxybenzoate group. The  $\sigma$ -form Ag $\cdots$ C supramolecular bond bridges [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub> units into an infinite 2D layered polymer [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub>. The coordination sphere of the silver atom is best described as a distorted T-shaped geometry.

**Keywords**    hydrothermal reaction, Ag(I) complex, supramolecular polymer, TG-DTG

### Introduction

Supramolecular chemistry may be defined as “chemistry beyond the molecule” bearing on the organized entities of higher complexity resulting from the association of two or more chemical species held together by intermolecular non-covalent forces, including hydrogen bond, electrostatic interaction, van der Waals force and short-range exclusion force, *etc.*<sup>1</sup> Supramolecular compounds with special structures and functions have wide application in various fields such as material, catalysis, conductor, semi-conductor, medicine, biotechnology.<sup>2,3</sup> In spite of that the d<sup>10</sup> monovalent ion group has received tremendous attention in the last twenty-five years, molecular and electronic structure studies of gold(I) complexes are only under ongoing investigation by several research groups. Recent work includes simple monomeric complexes<sup>4-6</sup> as well as dinuclear and polynuclear clusters of Au(I).<sup>7-9</sup> Similar coordination complexes of Cu(I) also have been thoroughly investigated for their structural and spectral properties.<sup>10-12</sup> But, silver is by far the least investigated coinage metal despite in the same group as copper and gold. Very few spectroscopic investigations have been reported for Ag(I) molecular coordination compounds. In addition, Rebello and Ram Reddy have assumed that carboxylate derivatives have many functions in medicine and agriculture, and their activities are due to the formation of chelated rings with metal ions.<sup>13</sup> For these reasons, our group began to synthesize various silver coordination compounds with carboxylate derivatives and

study their chemical properties. When we chose that sodium *o*-hydroxybenzoate reacted with AgNO<sub>3</sub> in hydrothermal reactions, [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub> was obtained. Here we report the synthesis, thermal stability and the crystal structure of supramolecular polymeric [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub>.

### Experimental

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses (C and H) were carried out on a Perkin-Elmer 240C analyzer. Electronic absorption spectra were obtained on a Shimadzu 3100 spectrophotometer in H<sub>2</sub>O/EtOH solution. Thermogravimetry (TG) and differential thermal gravimetric (DTG) analysis were recorded on an SDT 2980 simultaneously for the samples of 10 mg under a nitrogen atmosphere (150 mL/min) at a heating rate of 20  $^\circ$ C/min.

A mixture of *o*-HOPhCO<sub>2</sub>Na (0.16 g, 1.00 mmol), AgNO<sub>3</sub> (0.17 g, 1.00 mmol), and H<sub>2</sub>O (15 mL) was stirred and its pH value was adjusted to 6 with 90% *o*-HOPhCO<sub>2</sub>H. The slurry was generated, then sealed in a 25 mL stainless-steel reactor with Teflon liner at 140  $^\circ$ C for 72 h resulting in the formation of the brown crystals of the title complex. Yield 85%. Calcd for [Ag(*o*-HOPhCO<sub>2</sub>)]: C 34.32, H 2.88; found C 34.06, H 2.52. Electronic spectra,  $\lambda_{\max}$  300 nm, relates to the conjugation of the phenyl ring, carboxyl and hydroxyl group of *o*-hydroxyl benzoate.

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### Crystal structure determination

The data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda=0.071073$  nm). Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction was carried out using SADABS program.<sup>14</sup> The structure was solved by direct methods using SHELXS-97.<sup>15</sup> All the non-hydrogen atoms were refined on  $F^2$  anisotropically by full-matrix least squares method. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-Ray Crystallography.<sup>16</sup> Summaries of crystal and intensity collection for the title compound are given in Table 1.

**Table 1** Crystallographic data and structure refinement for the title compound

Empirical formula	C <sub>7</sub> H <sub>5</sub> AgO <sub>3</sub>
Formula weight	244.98
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a=0.73940(15)$ nm $b=0.88220(18)$ nm $\beta=107.66(3)^\circ$ $c=1.0662(2)$ nm
Volume	$0.6627(2)$ nm <sup>3</sup>
Z	4
Calculated density	$2.455$ Mg/m <sup>3</sup>
Absorption coefficient	$2.982$ mm <sup>-1</sup>
$F(000)$	472
Crystal size	$0.25$ mm $\times$ $0.15$ mm $\times$ $0.10$ mm
$\theta$ range for data collection	$2.89^\circ$ — $24.94^\circ$
Limiting indices	$0 \leq h \leq 8, 0 \leq k \leq 10, -12 \leq l \leq 12$
Reflections collected/unique	1262/1168 [ $R_{int}=0.0281$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	1168/0/100
Goodness-of-fit on $F^2$	1.310
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.0333, wR_2=0.1044$
$R$ indices (all data)	$R_1=0.0531, wR_2=0.1166$
Large diff. peak/hole	770, $-659$ e <sup>-</sup> nm <sup>-3</sup>

## Results and discussion

### Crystal structure of [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub>

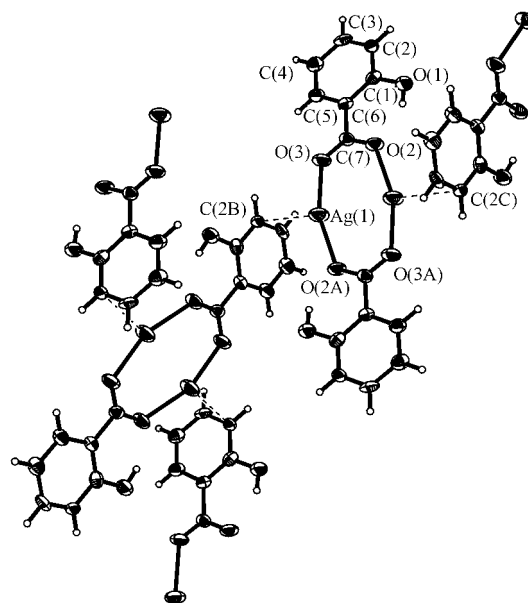
[Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub> was synthesized under hydrothermal conditions by reaction of sodium *o*-hydroxybenzoate with AgNO<sub>3</sub>. Single crystals suitable for X-ray analysis were obtained by slowly evapo-

rating from an aqueous solution at room temperature. Selected bond lengths and angles are given in Table 2, and an ORTEP diagram of the title compound is shown in Figure 1, and Figure 2 shows a perspective view of the crystal packing.

**Table 2** Selected bond lengths (nm) and angles ( $^\circ$ ) of the title compound

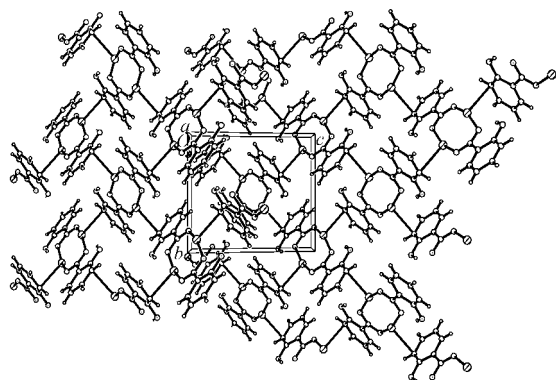
Ag(1)—O(2A)	0.2184(6)	O(1)—C(1)	0.1347(1)
Ag(1)—O(3)	0.2198(6)	O(2)—C(7)	0.1268(1)
Ag(1)—C(2B)	0.2678(8)	O(3)—C(7)	0.1232(1)
C(6)—C(7)	0.1505(1)	Ag(1)···Ag(1A)	0.2850(2)
O(2A)—Ag(1)—O(3)	159.6(3)	O(2A)—Ag(1)—Ag(1A)	80.70(2)
O(2A)—Ag(1)—C(2B)	107.8(2)	O(3)—Ag(1)—Ag(1A)	81.89(2)
O(3)—Ag(1)—C(2B)	87.0(3)	C(2B)—Ag(1)—Ag(1A)	164.61(2)
C(7)—O(2)—Ag(1A)	124.1(5)	C(7)—O(3)—Ag(1)	123.8(6)

Symmetry transformations used to generate equivalent atoms: B:  $-x, y+1/2, -z+3/2$ ; A:  $-x+1, -y, -z+2$ .



**Figure 1** Perspective view of [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub> at 50% probability.

In the title compound, four carboxyl oxygen atoms of two *o*-hydroxybenzoate groups bridge two silver(I) ions to form an eight-membered Ag<sub>2</sub>O<sub>4</sub>C<sub>2</sub> ring. The silver(I) atom is two-coordinated by two carboxylic oxygen atoms of two *o*-hydroxybenzoate ligands, and meanwhile, forms a supramolecular interaction with one carbon atom of phenyl-ring in the third *o*-hydroxybenzoate group. The  $\sigma$ -form Ag···C supramolecular action bridges [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub> units into an infinite 2D layered polymer [Ag<sub>2</sub>(*o*-HOPhCO<sub>2</sub>)<sub>2</sub>]<sub>n</sub>. The coordination sphere of the silver atom is best described as a distorted T-shaped geometry.<sup>17</sup> The bond angles of O(2A)—Ag(1)—O(3), O(3)—Ag(1)—C(2B) and O(2A)—

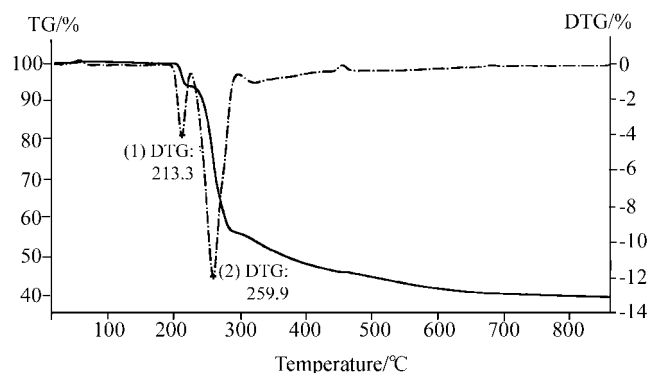


**Figure 2** A view of the crystal packing down the *a*-axis for the title compound.

Ag(1)-C(2B) are  $159.6(3)^\circ$ ,  $87.0(3)^\circ$  and  $107.8(2)^\circ$ , respectively. The Ag $\cdots$ C distance [0.2678(8) nm] is comparable with in those of Ag<sub>4</sub>(HPB)(ClO<sub>4</sub>)<sub>4</sub> (HPB = hexaphenylbenzene), in which the Ag—C distances are ranged from 0.2420(9) to 0.2750(1) nm.<sup>18</sup> The silver atom is asymmetrically coordinated to two oxygen atoms with Ag—O distances of 0.2184(6) and 0.2198(6) nm, which are the average distances compared with those found in the similar coordination environment of Ag(I), such as {[Ag<sub>2</sub>(β-ala)<sub>2</sub>(NO<sub>3</sub>)]NO<sub>3</sub>]<sub>n</sub> (β-ala = β-alanine) [0.2147(5)—0.2287(5) nm].<sup>17</sup> The Ag $\cdots$ Ag distance is 0.2850(2) nm, which is longer than those observed in bis(μ-*N,N'*-η<sup>2</sup>-*N,O*-η<sup>2</sup>-*N',O'*-di(*o*-methoxyphenyl)formamidinato)disilver(I) [0.2783(1) nm]<sup>19</sup> and bis[*N,N'*-di(*p*-tolyl)formamidinato]disilver(I) [0.2705(1) nm],<sup>20</sup> but shorter than those reported for disilver compounds supported by phosphine ligands [0.2890—0.3095 nm].<sup>21</sup> Here the Ag $\cdots$ Ag distance is shorter than twice Van der Waals radius of Ag(I), also it is less than twice the radius of metallic 12-coordinate for silver (0.288 nm),<sup>17</sup> so we know that there exists an interaction between two Ag(I) atoms. The phenyl ring with the conjunction of C(7), O(1) and O(2) atoms are fairly planar, the maximum deviation from the least squares plane is 0.0028(2) nm. Plane equation is  $-2.7931x + 5.7308y + 7.9250z = 1.6826$ .

### Thermogravimetric analysis

The curves of the thermogravimetric (TG) analysis and differential thermal gravimetric (DTG) analysis for the title compound are shown in Figure 3. It can be seen that the thermal decomposition of the compound includes three transitions. There are two endothermic peaks, one weak heat-absorbing peak at 213.3 °C and the other very intense peak at 259.9 °C. It shows no decomposition before 210 °C, but, at 213.3 °C, decomposition occurs. On the basis of weight changes in the TG curve, the first process of the weight loss (6.25%) corresponds to the loss of hydroxyl of phenyl ring (found 6.25%, calcd 6.56%) (210—223 °C), with weak endothermic phenomenon, and the second process of the weight loss (37.25%) is attributed to the loss of phenyl ring and a tertiary carbon atom of it (found



**Figure 3** TG/DTG curves of the title compound.

37.25%, calcd 36.07%) (238—294 °C). From the crystal structure, we think that the C—O bond breakage of benzoic acid group occurs here and because the endothermic peak is very intense, Ag—C bond breakage may also occur here. Finally, Ag<sub>2</sub>O<sub>4</sub> decomposes gradually (300—800 °C). The residue may be Ag atom (found 40.14%, calcd 44.26%).

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