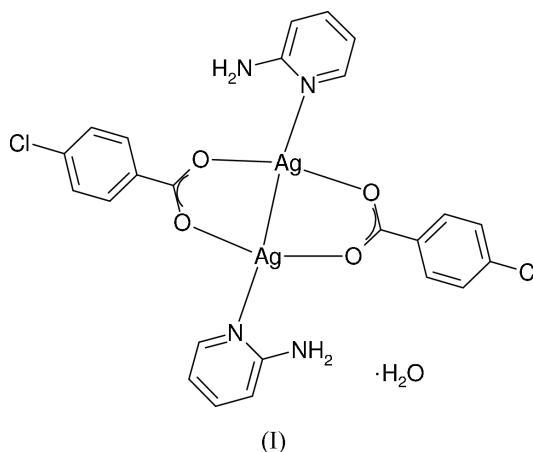


Bis(μ -4-chlorobenzoato- κ^2 O:O')bis[(2-aminopyridine- κ N)silver(I)](Ag—Ag) monohydrate**Zhong-Lu You,^{a,b} Hai-Liang Zhu^{a*} and Wei-Sheng Liu^b**^aDepartment of Chemistry, Fuyang Normal College, Fuyang Anhui 236041, People's Republic of China, and ^bDepartment of Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of ChinaCorrespondence e-mail:
hailiang_zhu@163.com**Key indicators**Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.053
 wR factor = 0.119
Data-to-parameter ratio = 16.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $[\text{Ag}_2(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_5\text{H}_6\text{N}_2)_2] \cdot \text{H}_2\text{O}$, lies about an inversion center, with the water molecule on a twofold rotation axis, and the Ag^{I} atom is three-coordinated by two O atoms from two different but symmetry-related 4-chlorobenzoate anions and one N atom from one 2-aminopyridine ligand. The 4-chlorobenzoate anion acts as a bidentate ligand, bridging two inversion-related Ag atoms of the complex and forming a dimer. In the crystal structure, the molecules are linked through intramolecular and intermolecular $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, forming two-dimensional layers parallel to the bc plane.

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The study of the variety of products in the self-assembly processes between labile metal ions and flexible multidentate ligands is an interesting topic in supramolecular chemistry (Khlobystov *et al.*, 2001; Zheng *et al.*, 2003; Xu *et al.*, 2001; Santra *et al.*, 2001; Zhu, Liu *et al.*, 2003). The balance between the formation of different structures is often subtle. Factors that affect the coordination polymer topology include not only the highly influential forces of metal and ligand coordination preferences but also the ambient conditions. The latter factor is very important, but to our knowledge, seldom investigated.



Recently, we have reported a dinuclear silver(I) complex with 2-aminopyridine and silver(I) 4-chlorobenzoate as the starting materials, namely bis(μ -4-chlorobenzoato- κ^2 O:O')bis[(2-aminopyridine- κ N)silver(I)] [(II); Zhu *et al.*, 2004], which was crystallized at room temperature. In order to study the effects of temperature in the crystallization of the silver(I) complex, in this paper, we use the same starting materials as described for (II) to synthesize a different crystal structure of the title compound at 273 K.

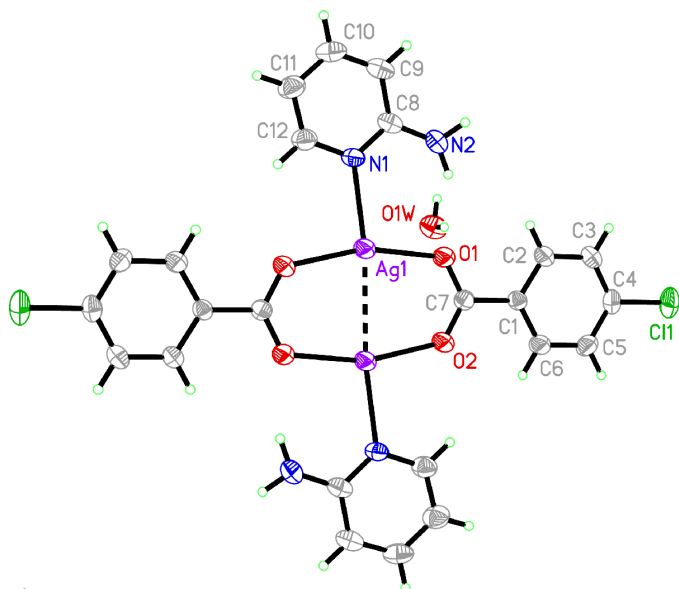


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The title compound, (I), consists of a dinuclear silver(I) complex on an inversion center and a solvent water molecule on a twofold rotation axis (Fig. 1). In the dinuclear silver(I) complex, each Ag ion is three-coordinated by two O atoms from two different but symmetry-related 4-chlorobenzoate anions and one N atom from one 2-aminopyridine ligand. It should be noted that the Ag–Ag distance (Table 1) is approximately equal to that in metallic silver, indicating an apparent Ag–Ag bond (Zhu, Zhang *et al.*, 2003). Ignoring the Ag–Ag bond, the AgO₂N coordination forms an approximately T-shaped geometry at Ag1, with the three angles subtended at the Ag atom being 162.59 (12), 95.17 (13) and 102.05 (13)°, while in (II), there is a Y-shaped geometry at Ag1. This is caused by the larger strain of the four-membered ring in (II) than that of the eight-membered ring in (I), as well as the strong Ag–Ag interaction in (I), which is very weak in (II). We deduce that the lower strain and the stronger Ag–Ag interactions in (I) compared to those in (II) are probably caused by the crystallization at low temperature, which leads to a slower crystallization process and causes the crystal structure to be more stable.

The Ag1–O1 bond length is a little longer than Ag1–O2ⁱ [symmetry code: (i) 2 – x, 1 + y, $\frac{3}{2}$ – z], which is caused by the intramolecular N2–H2B···O1 hydrogen bond. The intramolecular hydrogen bond decreases the electron density around O1, and weakens the coordinate bond between Ag1 and O1. The Ag1–N1 bond length is much longer than the value of 2.137 (4) Å observed in (II), which is probably caused by the larger hindrance of the T-shaped Ag ion in (I) for the 2-aminopyridine group than that of the corresponding Y-shaped Ag ion in (II). All other bond lengths in (I) are within normal ranges (Allen *et al.*, 1987).

Through the strong interactions between the two Ag ions, the eight-membered ring Ag1/O1/C7/O2/Ag1ⁱ/O1ⁱ/C7ⁱ/O2ⁱ is severely compressed. As required by the crystallographic

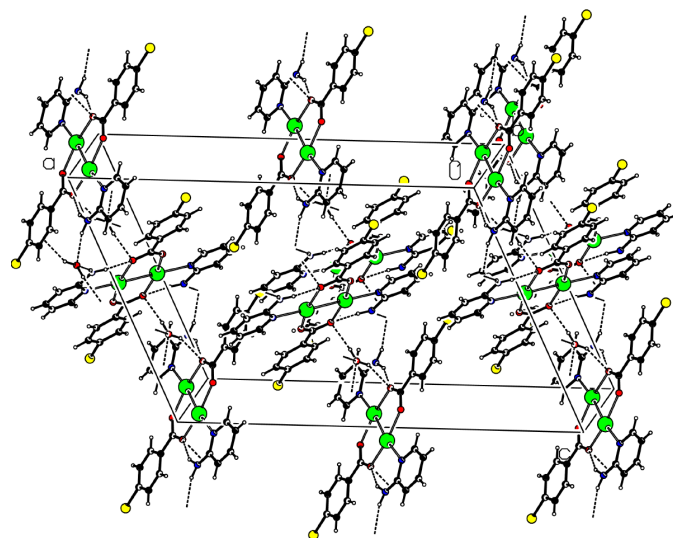


Figure 2
View of (I) (Spek, 2004), showing intramolecular and intermolecular N–H···O and O–H···O hydrogen bonds as dashed lines. Color codes: green Ag, yellow Cl, red O, blue N and black C.

symmetry, the atom Ag1 lies in the O1/O2/O1ⁱ/O2ⁱ plane. The dihedral angle between the pyridine ring of the 2-aminopyridine group and the benzene ring of the 4-chlorobenzoate anion is 3.9 (8)°.

In the crystal structure of (I), the molecules are linked through intramolecular and intermolecular N–H···O and O–H···O hydrogen bonds (Table 2), forming two-dimensional layers parallel to the *bc* plane (Fig. 2).

Experimental

Ag₂O (0.1 mmol, 23.2 mg) and 4-chlorobenzoic acid (0.2 mmol, 31.4 mg) were dissolved in a 30% aqueous ammonia solution (10 ml), and the resulting solution was stirred for *ca* 10 min to give a clear colorless solution. After the solution had cooled to 273 K, a cooled solution of 2-aminopyridine (0.1 mmol, 9.4 mg) in acetonitrile (3 ml) was added. The mixture was then stirred for 1 h, and the resulting colorless solution was kept in a refrigerator for 10 d. Colorless block-shaped crystals formed with slow evaporation of the solvent.

Crystal data

[Ag₂(C₇H₄ClO₂)₂(C₅H₆N₂)₂]·H₂O
M_r = 733.10
 Monoclinic, *C*2/*c*
a = 27.387 (2) Å
b = 5.504 (3) Å
c = 17.879 (2) Å
 β = 103.630 (2)°
V = 2619.2 (15) Å³
Z = 4

D_x = 1.859 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 1127 reflections
 θ = 2.4–23.6°
 μ = 1.74 mm^{−1}
T = 293 (2) K
 Block, colorless
 0.15 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.780, *T_{max}* = 0.845
 13354 measured reflections

2843 independent reflections
 2598 reflections with *I* > 2σ(*I*)
R_{int} = 0.033
 θ_{max} = 27.0°
h = −34 → 34
k = −7 → 7
l = −22 → 22

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.119$
 $S = 1.23$
 2843 reflections
 168 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 4.3842P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.81 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ag1—O2 ⁱ	2.207 (3)	Ag1—N1	2.352 (3)
Ag1—O1	2.233 (4)	Ag1—Ag1 ⁱ	2.8913 (17)
O2 ⁱ —Ag1—O1	162.59 (12)	O1—Ag1—N1	102.05 (13)
O2 ⁱ —Ag1—N1	95.17 (13)		

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2A \cdots O1W ⁱⁱ	0.90 (4)	2.17 (4)	3.037 (6)	162 (4)
N2—H2B \cdots O1	0.89 (4)	2.17 (2)	3.009 (6)	156 (5)
O1W—H1W \cdots O1	0.88 (5)	2.09 (6)	2.892 (4)	151 (6)

Symmetry code: (ii) $x, y - 1, z$.

Atoms H2A and H2B were located in a difference Fourier map and refined isotropically, with the N—H and H \cdots H distances restrained to 0.90 (1) and 1.41 (2) \AA , respectively. Atom H1W was also located in a difference Fourier map and refined isotropically, and the $U_{\text{iso}}(\text{H})$ value fixed at 0.08 \AA^2 . The other H atoms were placed in

idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.93 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXTL.

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References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bruker (1998). SHELXTL (Version 5.1), SMART (Version 5.628) and SAINT (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
- Khlobystov, A. N., Blake, A. J., Champness, N. R., Lemenovskii, D. A., Majouga, A. G., Zyk, N. V. & Schröder, M. (2001). *Coord. Chem. Rev.* **222**, 155–192.
- Santra, P. K., Ray, U., Pal, S. & Sinha, C. (2001). *Inorg. Chem. Commun.* **4**, 269–273.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Xu, A.-W., Su, C.-Y., Zhang, Z.-F., Cai, Y.-P. & Chen, C.-L. (2001). *New J. Chem.* **25**, 479–482.
- Zheng, S.-L., Zhang, J.-P., Wong, W.-T. & Chen, X.-M. (2003). *J. Am. Chem. Soc.* **125**, 6882–6883.
- Zhu, H.-L., Liu, X.-Y., Wang, X.-J., Yang, F., Usman, A. & Fun, H.-K. (2003). *Z. Anorg. Allg. Chem.* **629**, 1986–1990.
- Zhu, H.-L., Qiu, X.-Y., Yang, S., Shao, S.-C., Ma, J.-L. & Sun, L. (2004). *Acta Cryst. C* **60**, m170–m171.
- Zhu, H.-L., Zhang, X.-M., Liu, X.-Y., Wang, X.-J., Liu, G.-F., Usman, A. & Fun, H.-K. (2003). *Inorg. Chem. Commun.* **6**, 1113–1116.