

**Bis(μ -4-chlorobenzoato- κ^2 O:O)bis-
[(2-aminopyridine- κ N)silver(I)]****Hai-Liang Zhu,* Xiao-Yang Qiu, Song Yang, Si-Chang
Shao, Ji-Long Ma and Lin Sun**Department of Chemistry, Fuyang Normal College, Fuyang, Anhui 236041, People's
Republic of China

Correspondence e-mail: hailiang_zhu@fync.edu.cn

Received 4 February 2004

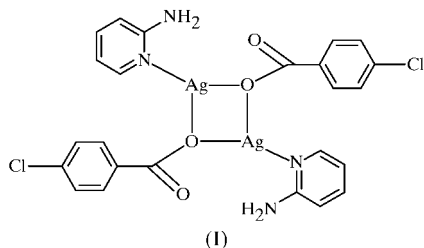
Accepted 16 February 2004

Online 11 March 2004

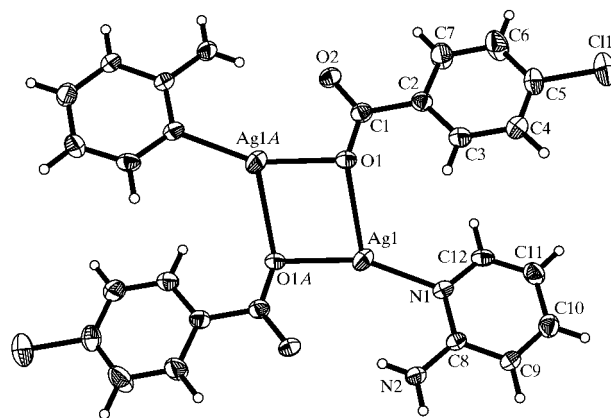
The title compound, $[\text{Ag}_2(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_5\text{H}_6\text{N}_2)_2]$, lies about an inversion centre and the Ag atom is three-coordinated by two O atoms and one N atom from three different ligands. The 4-chlorobenzoate anion acts as a monodonor ligand, bridging two inversion-related Ag atoms of the compound into a dimer. There are weak intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds in the structure.

Comment

Pyridine and its derivative metal complexes are of much current interest in coordination chemistry. Indeed, many monomers, dimers and polymers have been prepared and structurally determined. Recently, we reported a few silver(I) complexes with pyridine and pyridine derivatives (Zhu *et al.*, 2001, 2003a; Zhu, Liu *et al.*, 2003; Zhu, Yang *et al.*, 2003; Zhu, Zhang, Sun *et al.*, 2003; Zhu, Zeng *et al.*, 2003). Some of the complexes (Zhu *et al.*, 2001) have high cytotoxicity. To further our work in this field, we report here the crystal structure of the title silver-carboxylate complex, (I), with 2-aminopyridine.



In compound (I), the Ag atom is three-coordinated by two O atoms from different 4-chlorobenzoate anions and one N atom from the 2-aminopyridine ligand. This AgO_2N coordination forms a Y-shaped geometry at Ag1, with the three angles subtended at the Ag atom being 82.80 (12), 120.37 (12) and 156.79 (13)°. The Ag1—O1 bond length of 2.589 (3) Å is much longer than that in bis[aqua(4-chlorobenzoato)silver(I)]

**Figure 1**

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with the suffix A are at the symmetry position ($2-x, -y, -z$).

[2.103 (5) Å; Zhu *et al.*, 2003b], but is close to that found in 4-fluorobenzoatosilver(I) [2.512 (4) Å; Zhu, Zeng *et al.*, 2003]. The Ag—N bond length [2.137 (4) Å] is comparable with those in similar silver complexes with pyridine derivatives that we have investigated. All other bond lengths (Table 1) in (I) are within normal ranges (Allen *et al.*, 1987).

Some pyramidalization is shown by atom O1, which is 0.407 (3) Å out of the plane through atoms C1, Ag1 and Ag1ⁱ [symmetry code: (i) $2-x, -y, -z$]. The two exocyclic angles about O1 are strongly asymmetric, with Ag1—O1—C1 of 138.0 (3)° being much larger than Ag1ⁱ—O1—C1 of 107.6 (3)°, and this seems to be caused by the $\text{N2}-\text{H2}\cdots\text{O2}^i$ attraction on one side and the $\text{H3}\cdots\text{H12}$ steric repulsion on the other. As is shown in (I), the benzoate carboxyl group acts as a monodonor bridging two Ag atoms, forming the title dimeric dinuclear complex.

The central Ag_2O_2 four-membered coordination ring has a rectangular geometry, with the Ag1—O1 distance of 2.589 (3) Å being noticeably longer than Ag1—O1ⁱ of 2.191 (3) Å. The O1—Ag1—O1ⁱ bond angle must be related to the Ag1—O1—Ag1ⁱ angle and the planarity of the central ring, while the asymmetry of the exocyclic bond angles about Ag1 is related to the planarity of the bonds to Ag and the different interactions in which the two sides of the amino-pyridine ligand are involved, namely the $\text{H1}\cdots\text{H12}$ (2.71 Å) contact on the side of the narrower O1—Ag1—N1 [120.4 (1)°] angle and the $\text{N2}-\text{H2A}\cdots\text{O2A}$ intramolecular hydrogen bond on the side of the larger N1—Ag1—O1ⁱ [156.8 (1)°] angle. The ring is on a plane which makes a dihedral angle of 42.4 (2)° with benzene and 38.1 (2)° with pyridine; the two aromatic rings are approximately coplanar, the dihedral angle they form being only 12.4 (2)°. The displacement from perfect coplanarity is probably caused by steric hindrance between the two organic ligands, which is also related to the more pronounced displacement from coplanarity which these ligands show with respect to the central coordination ring.

The intramolecular $\text{C3}-\text{H3}\cdots\text{O1}$ and $\text{C7}-\text{H7}\cdots\text{O2}$ interactions, the $\text{H}\cdots\text{O}$ distances of which are significantly less

than the sum of the van der Waals radii, are remarkable for the conformation of the anionic ligand. In the crystal structure of (I), the molecules are interconnected, in columns parallel to the *b* axis, by intermolecular N2—H2B—O2ⁱⁱ and N2—H2A···O2ⁱ hydrogen bonds [Table 2; symmetry code: (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$].

Experimental

Ag₂O (0.5 mmol, 116 mg) and 4-chlorobenzoic acid (1 mmol, 157 mg) were dissolved in a 30% aqueous ammonia solution (10 ml), and the resulting solution was stirred for *ca* 10 min until a clear solution was obtained. A solution of 2-aminopyridine (1 mmol, 94 mg) in acetonitrile (2 ml) was added to the above solution. The resulting solution was kept in air for 2 d with ammonia gas escaping. Colourless crystals of (I) were collected and washed with water and acetonitrile in turn, and then dried in a vacuum desiccator over CaCl₂ (yield 44%). Analysis calculated for C₁₂H₁₀AgClN₂O₂: C 40.31, H 2.82, N 7.83%; found: C 39.95, H 2.88, N 7.69%.

Crystal data

[Ag ₂ (C ₇ H ₄ ClO ₂) ₂ (C ₅ H ₆ N ₂) ₂]	Mo K α radiation
<i>M_r</i> = 715.08	Cell parameters from 1840 reflections
Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	θ = 2.8–22.2°
<i>a</i> = 14.366 (5) Å	μ = 1.84 mm ^{−1}
<i>b</i> = 5.545 (2) Å	<i>T</i> = 298 (2) K
<i>c</i> = 15.530 (6) Å	Prism, colourless
β = 92.360 (6)°	0.42 × 0.30 × 0.09 mm
<i>V</i> = 1236.0 (8) Å ³	
<i>Z</i> = 2	
<i>D_x</i> = 1.921 Mg m ^{−3}	

Data collection

Siemens SMART CCD area-detector diffractometer	2179 independent reflections
φ and ω scans	1566 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.038
<i>T</i> _{min} = 0.512, <i>T</i> _{max} = 0.852	θ_{max} = 25.0°
5997 measured reflections	<i>h</i> = −17 → 17
	<i>k</i> = −5 → 6
	<i>l</i> = −15 → 18

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.111$	$(\Delta/\sigma)_{\text{max}} = 0.001$
<i>S</i> = 0.99	$\Delta\rho_{\text{max}} = 0.58 \text{ e Å}^{-3}$
2179 reflections	$\Delta\rho_{\text{min}} = -0.81 \text{ e Å}^{-3}$
163 parameters	
H-atom parameters constrained	

All H atoms were placed in geometric positions and constrained to ride on their parent atoms, with N—H and C—H distances of 0.90 and 0.96 Å, respectively, and *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.2*U*_{eq}(N).

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to

Table 1

Selected geometric parameters (Å, °).

Ag1—N1	2.137 (4)	Ag1—O1	2.589 (3)
Ag1—O1 ⁱ	2.191 (3)		
N1—Ag1—O1 ⁱ	156.79 (13)	O1 ⁱ —Ag1—O1	82.80 (12)
N1—Ag1—O1	120.37 (12)		

Symmetry code: (i) 2 − *x*, −*y*, −*z*.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2A···O2 ⁱ	0.86	2.29	3.141 (5)	170
N2—H2B···O2 ⁱⁱ	0.86	2.16	2.990 (5)	163
C3—H3···O1	0.93	2.49	2.789 (6)	99
C7—H7···O2	0.93	2.52	2.815 (7)	99

Symmetry codes: (i) 2 − *x*, −*y*, −*z*; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

The authors thank the Education Office of Anhui Province, People's Republic of China, for research grant No. 2004kj300zd, and the Natural Science Foundation of Hubei Province, People's Republic of China, for research grant No. 2003ABB010.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1642). Services for accessing these data are described at the back of the journal.

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