metal-organic papers

(μ-Biphenyl-4,4′-dicarboxylato)bis[(2-amino-pyridine)silver(I)]

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The title compound, $[Ag_2(C_{14}H_8O_4)(C_5H_6N_2)_2]$, is a dinuclear Ag^I complex which has crystallographic inversion symmetry. Each Ag atom is three-coordinated by two N atoms from two 2-aminopyridine ligands and by one O atom from a biphenyl-4,4′-dicarboxylate ligand, giving a Y-shaped coordination environment. Two Ag^I atoms are linked through a biphenyl-4,4′-dicarboxylate ligand, acting as a bridge, forming a dimeric complex. The separation between the two silver(I) centres is 15.879 (3) Å. In the crystal structure, molecules are connected by N—H···O hydrogen bonds, forming molecular tapes in the a-axis direction.

Comment

Metal complexes of pyridine and its derivatives are of much current interest in coordination chemistry. Indeed, many monomers, dimers and polymers have been prepared and structurally determined. Recently, we have reported two dimeric silver(I) complexes with 2-aminopyridine and different counter-anions, *viz.* bis(μ-2-aminopyridine)bis[(trifluoroacetato)silver(I)], (II) (You & Zhu, 2004), and bis(μ-4-chlorobenzoato-κ^2O:O)bis[(2-aminopyridine-κN)silver(I)], (III) (Zhu *et al.*, 2004). In order to discover how the counter-anions affect the construction of silver(I) coordination dimers with 2-aminopyridine, we report here the crystal structure of the title dimeric silver(I) complex, (I).

(I)
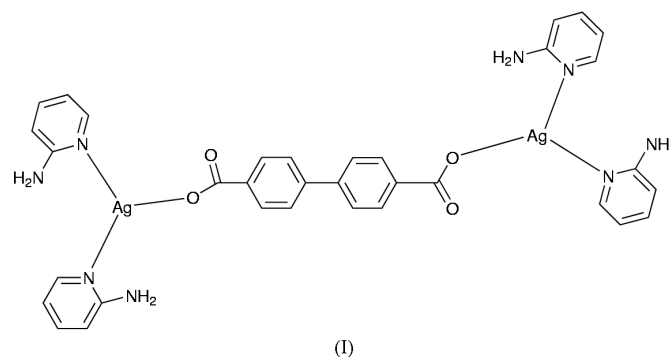
In (I), each Ag atom is three-coordinated by two N atoms from two 2-aminopyridine ligands and by one O atom from a biphenyl-4,4′-dicarboxylate ligand, giving a Y-shaped coordination environment (Table 1), the biphenyl-4,4′-dicarboxylate ligand acting as a bridge, forming a dimeric complex (Fig. 1). The complex has crystallographic inversion symmetry. The Ag—N bond lengths [2.214 (3) and 2.253 (3) Å] are comparable with those in (II) [2.137 (4) Å] and (III) [2.269 (3) Å]. The structure of (I) is linear and very different from that of

(II) and (III). In (II) and (III), the Ag^I atoms are linked through coordinated atoms, forming four-membered and eight-membered rings, respectively. The differences between the complexes is probably caused by the presence of different counter-anions. We infer that, in order to give three-coordinated silver (I), a bridging ligand is required that can not chelate.

The separation between the two silver(I) centres is 15.879 (3) Å. In the crystal structure, the molecules are connected through N—H···O hydrogen bonds to form tapes in the a-axis direction (Fig. 2).
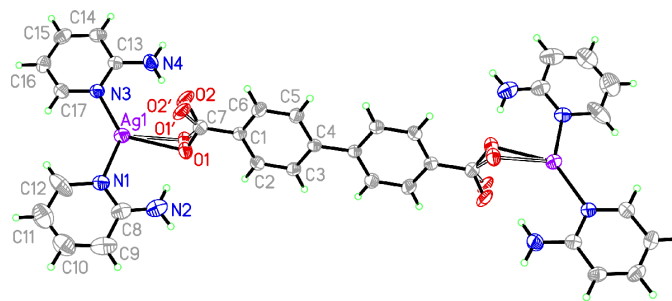

Figure 1
View of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. The minor disorder component is shown with open bonds. Unlabelled atoms are related by the symmetry code $(1 - x, -y, -z)$.

Experimental

Ag$_2$O (0.5 mmol, 116 mg) and biphenyl-4,4′-dicarboxylic acid (1 mmol, 242 mg) were dissolved in a 30% aqueous ammonia solution (10 ml), and the resulting solution was stirred for ca 30 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 10 d with ammonia gas escaping. Colourless crystals of (I) were collected and washed with water, and then dried in a vacuum desiccator over CaCl$_2$ (yield 61%). Analysis calculated for C$_{34}$H$_{32}$Ag$_2$N$_8$O$_4$: C 49.31, H 3.82, N 13.40%; found: C 49.06, H 3.87, N 13.46%.

Crystal data

[Ag$_2$(C$_{14}$H$_8$O$_4$)(C$_5$H$_6$N$_2$)$_2$]
$M_r = 832.42$
Monoclinic, $P2_1/n$
$a = 5.9220$ (8) Å
$b = 24.946$ (3) Å
$c = 11.1751$ (14) Å
$\beta = 97.761$ (2)°
$V = 1635.8$ (4) Å^3
$Z = 2$

$D_x = 1.690$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3559 reflections
$\theta = 4.6–28.4°$
$\mu = 1.25$ mm^{-1}
$T = 298$ (2) K
Block, colourless
$0.12 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.865$, $T_{max} = 0.907$
9103 measured reflections

3559 independent reflections
2834 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.0°$
$h = -6 \rightarrow 7$
$k = -31 \rightarrow 19$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.129$
$S = 1.03$
3559 reflections
236 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 1.6038P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

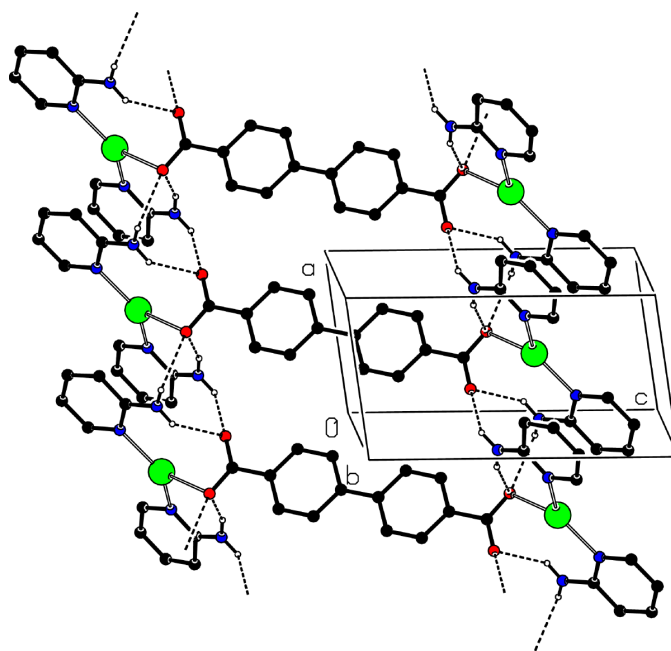|			
Ag1—N3	2.214 (3)	Ag1—O1	2.419 (12)
Ag1—N1	2.253 (3)		
N3—Ag1—N1	135.77 (13)	N1—Ag1—O1	100.4 (3)
N3—Ag1—O1	123.5 (3)		

Figure 2
The crystal packing of (I), showing N—H···O hydrogen-bonding interactions as dashed lines. The minor component of disorder has been omitted. Colour codes: green Ag, red O, blue N and black C.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1	0.86	2.14	2.948 (12)	157
N2—H2B···O2^i	0.86	2.27	2.880 (6)	127
N4—H4A···O2	0.86	2.24	2.968 (11)	142
N4—H4B···O1^{ii}	0.86	2.47	2.907 (7)	112

Symmetry codes: (i) $1 + x, y, z$; (ii) $x - 1, y, z$.

Atoms O1 and O2 are disordered over two positions (O1/O1′ and O2/O2′) with occupancies of 0.69 (2):0.31 (2). This corresponds to rotational disorder about the C1—C7 bond. Geometric details of only the major component of disorder are included in Tables 1 and 2. All H atoms were placed in geometrically idealized positions (C—H = 0.93 Å and N—H = 0.86 Å) and allowed to ride on their parent atoms, with U_{iso}(H) = $1.2U_{eq}$(C and N)

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