Crystal Structure of Catena-poly [aqua silver(I)- μ -[1,4-diazabicyclo[2.2.2]*m*-fluorobenzoate dihydrate]

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The reaction of *m*-fluorobenzoate silver with a self-assembling system ligand (Dabco = 1,4-diazabicyclo[2.2.2]octane) in an acetonitrile–water (2:1) solution (10 ml) afforded a polymeric Ag(I) complex, {[Ag(H₂O)(Dabco)_{1.5}][C₇H₄FO₂] $\cdot$ 2H₂O]}_n, in high yield. X-ray crystallography was used to investigate the resulting Ag(I) complex. The coordination number around each Ag(I) is four, with a distorted tetrahedron geometry. Each silver cation is coordinated by three nitrogen atoms from three Dabco ligands and a water oxygen atom. Two silver cations are triconnected by three different Dabco ligands alternately into an infinite honeycomb-like layer on the *ac* plane. This complex was solved in the monoclinic system, space group *C2/c*, with the following unit-cell parameters: *a* = 21.461(6) Å, *b* = 14.919(4) Å, *c* = 12.319(3) Å, β = 90.000(3)°, *Z* = 8, *V* = 3944.1(18) Å³. The final *R* value was 0.0836 for 3834 measured reflections.

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The crystal engineering of coordination polymers has attracted great attention in recent years due to their potential as functional materials as well as their interesting compositions and topologies.^{1,2} Although general and precise principles for controlling the solid structures of the target products still need to be classified and established, many rational synthetic strategies have been brought forward and proved to be significant in the approach of designing the metal-based coordination supermolecules. The selection of proper ligands as “building blocks” is undoubtedly a key point in manipulating the network structure frameworks. Triethylene-diamine is a bidentate ligand that can coordinate to metal ions *via* two N atoms. It has a very versatile coordination behavior, since it can form bridges between metallic centers, while generating varied and sometimes surprising molecular architectures.³ Recently, a polynuclear Ag^I complex with triethylenediamine as the ligand and a nitrite anion as a counter-anion, *viz* [Ag(NO₂)(C₆H₁₂N₂)(H₂O)]_n, has been reported.⁴ In order to

study the effects of the counter-anion in the construction of silver(I) coordination polymers, the title novel complex (I) is reported here.

The title complex, catena-poly [aqua silver(I)- μ -[1,4-diazabicyclo[2.2.2] *m*-fluorobenzoate dihydrate] (Fig. 1), was

Fig. 1 Chemical structure of the title complex (I).

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Table 1 Crystal and experimental data

CCDC No.	284257
Empirical formula	AgC ₁₆ H ₂₈ FN ₃ O ₅
Formula weight	469.28
Crystal system	monoclinic <i>Z</i> = 8
Space group	<i>C2/c</i> (15#)
<i>a</i> = 21.461(6) Å	
<i>b</i> = 14.919(4) Å	β = 90.000(3)°
<i>c</i> = 12.319(3) Å	
<i>V</i> = 3944.1(18) Å ³	<i>D</i> _{calc} = 1.581 g/cm ³
μ (Mo <i>K</i> α)	0.128 mm ⁻¹
Radiation (Mo <i>K</i> α)	0.71069 Å
<i>F</i> (0 0 0)	1928
θ range for data collection	1.66 to 25.99°
Completeness	0.99
Goodness-of-fit on <i>F</i> ²	1.116
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0640 <i>wR</i> ₂ = 0.1479
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0836 <i>wR</i> ₂ = 0.1580
($\Delta\rho$) _{max} = 1.169 eÅ ⁻³	($\Delta\rho$) _{min} = -0.719 eÅ ⁻³
<i>R</i> (int) = 0.0648	<i>R</i> (sigma) = 0.0719
No. of reflections measured	3834
No. of reflections used	3055
No. of parameters	325
Measurement	Bruker Smart Apex CCD diffractometer
Program system	SAINT
Structure determination	direct methods (SHELXS-97)
Refinement	full matrix least-squares (SHELXL-97)

Fig. 2 Molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only one orientation of the disordered Dabco species is shown. The H atom was omitted for clarity. The atom labeled with the suffix A is at the symmetry position $(0.5 - x, 0.5 - y, 1 - z)$.

Fig. 3 Packing diagram of (I), viewed along the c axis. Hydrogen bonds are indicated by broken lines.

prepared by dissolving *m*-fluorobenzoate silver (1 mmol, 247 mg) and 1,4-diazabicyclo[2.2.2]octane (1 mmol, 112 mg) in an acetonitrile-water (2:1) solution (10 ml), the mixture was stirred for about 40 min at room temperature. The resulting clear colorless solution was kept in air after slow evaporation of the solvent over a period of one week, large colorless crystals of (I) suitable for an X-ray diffraction study formed at the bottom of the vessel. Elemental analysis for $C_{16}H_{28}AgFN_3O_3$: Calcd. C 40.95, H 6.01, N 8.95%. Found C 40.53, H 6.24, N 8.24%.

X-ray data of a colorless crystal of $\{[Ag(H_2O)(Dabco)_{1.5}][C_7H_4FO_2] \cdot 2H_2O\}_n$ were collected on a Bruker Smart Apex CCD diffractometer ($\lambda = 0.71069$ Å) at 293 K. Because attempts to find a suitable orthorhombic space group failed, the structure was refined in the monoclinic space group $C2/c$, and was solved by direct methods and refined by full-matrix least squares with anisotropic temperature factors for the non-hydrogen atoms. The C atoms and their attached H atoms of the Dabco molecule were modeled as disordered over two positions with the symmetry constrained to equal occupancies. All of the other H atoms were placed at idealized positions and constrained to ride on their parent atoms, $U_{iso}(H) = 1.2$ -times its parent atom. The final difference map had peaks of less than 1.5 eÅ^{-3} near the Ag(1) atoms. The software used to prepare the material for publication was SHELXS-97.⁵ Table 1 summarizes the crystal and experimental data. The molecular structure is shown in Fig. 2. Selected bond lengths and bond angles are

Table 2 Bond lengths (Å) and angles (°) for complex (I)

Ag(1)-N(3)	2.312(5)
Ag(1)-N(1)	2.317(4)
Ag(1)-N(2)	2.322(5)
Ag(1)-OW3	2.576(4)
N(3)-Ag(1)-N(1)	120.19(16)
N(3)-Ag(1)-N(2)	118.21(16)
N(1)-Ag(1)-N(2)	116.97(17)
N(3)-Ag(1)-OW3	95.97(15)
N(1)-Ag(1)-OW3	100.99(16)
N(2)-Ag(1)-OW3	96.72(16)

Estimated standard deviation in the least-significant figure are given in parentheses.

listed in Table 2.

The structure of complex (I) consists of two-dimensional infinite cationic layers of a hexagonal network, *m*-fluorobenzoate anions and lattice water intercalating between the two-dimensional layers, as illustrated in Fig. 2 (the packing diagram (Fig. 3.)) The smallest repeat unit for the complex contains the $Ag(I)(H_2O)(Dabco)_{1.5}$ cation, one *m*-fluorobenzoate anion and two lattice water molecules (Scheme 1). *m*-Fluorobenzoate anions do not coordinate to silver, but act as counter-anions. The central Ag(I) ion shows a tetrahedral arrangement, being coordinated by three nitrogen atoms from three dabco ligands and an O atom of the aqua ligand. The Ag-N distances, 2.312(5) to 2.322(5) Å, are a slightly longer than those in related complexes for iazabicyclo[2,2,2]octane-Ag(I) complex, previously reported by us.⁴ The L-Ag-L angles are in the range of 95.97(15)° to 120.19(16)°, which shows a significant deviation from an angle of 109.5° for an ideal tetrahedron. The Ag-O distance, 2.576(4) Å is longer than that of the sum of the covalent radii for the Ag and O atoms, which is 2.27 Å.⁶ The shorter triethylene diamine-bridged two silver(I) atoms are separated by a distance of 7.208(5) Å. Each silver center is triconnected by three different Dabco ligands, and this linking way results in infinite planar sheets with hexagonal cavities on the ac plane. Each hexagonal unit is organized by six Ag(I) ions and six dabco molecules, each at the corner and midpoint of the side, respectively, while the *m*-fluorobenzoate anions and lattice water are located between these layers.

There are several O-H...O hydrogen bonds linking adjacent layers to form a three-dimensional network, such as: OW2-HW2A...O2 ($-x + 1/2, y - 1/2, -z + 1/2$) 2.824(8) Å; OW3-HW3A...O2 ($x, y - 1, z$) 2.815(7) Å; OW3-HW3B...O1 ($x, -y + 1, z + 1/2$) 2.831(7) Å; OW1-HW1A...OW2 ($-x + 1/2, -y + 1/2, -z$) 2.798(10) Å.

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