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Self-assembly of silver(I) coordination polymers with novel layered open network structures based on a flexible double betaine ligand†

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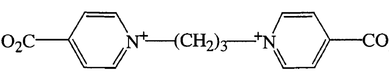
Three coordination polymers, $[Ag_4(L^1)_2(NO_3)_4]\cdot H_2O$ (**1**), $[Ag(L^1)](BF_4)\cdot 2H_2O$ (**2**) and $[Ag_2(L^1)(H_2O)](ClO_4)_2$ (**3**), were obtained from self-assembly of AgX (X = NO_3^-, BF_4^-, or ClO_4^-) with a new flexible double betaine L^1 (L^1 = 1,3-bis-(pyridinio-4-carboxylato)propane). Single crystal X-ray diffraction studies for complexes **1**–**3** reveal layered open network structures containing novel cavities and channels. Complex **1** consists of an unprecedented rhombic tetrameric Ag_4O_2 subunit, in which a μ_3-η^1 coordination mode of the carboxylate group is found for the first time among silver(I) carboxylates. Complex **2** is constructed from a bis(carboxylate-*O*,*O′*)-bridged centrosymmetric dimeric subunit, in which the coordination sphere of each silver(I) atom is completed by a monodentate carboxylate group at each axial site. In complex **3**, the $[Ag_2(\text{carboxylate-}O,O')_2]$ dimeric subunits are extended into a polymeric chain through the linkage of each metal centre to carboxylate groups of an adjacent dimer, and such infinite chains are extended into a plane wave-like layer structure by the cross-linkage of the molecular skeletons of the flexible double betaine ligands.

Introduction

One of reasons for the recent intensive interest in the design and construction of coordination polymers with open structures is to develop a new family of microporous materials functioning as zeolites.[1,2] The size, shape, and function of cavities or channels in these polymeric frameworks can be controlled by selecting the chemical structure of the organic spacers and the coordination geometry of inorganic metal ion species.[2–6] A convenient way to open structures is to self-assemble rigid multifunctional bridging ligands and metal ions.[2–4] Based on the configuration of ligands and the coordination geometry of metal ions, architectures of the resulting coordination networks with regular pore shapes can be reasonably well predicted. However, the use of flexible or modified multifunctional ligands as building blocks has not been extensively investigated, which is expected to open a new door to engender coordination polymers with unusual porous structures.[5,6]

Our previous studies involve the generation of polymeric structures in metal dicarboxylate-like complexes by various double betaine ligands, each comprising two betaine functions (betaine: $Me_3N^+CH_2CO_2^-$).[7] Recent studies have shown that the variation of double betaine ligands regarding the type of bridging units, the flexibility of the molecular backbone and conformational preference, as well as the metal ions employed and their counter ions, has a profound influence on the polymeric structures obtained.[8–10] Herein, we report the self-assembly of a new double betaine ligand L^1 featuring a long flexible chain skeleton (L^1 = 1,3-bis(pyridinio-4-carboxylato)-propane) with different silver salts, which yields three novel two-dimensional non-interpenetrating open coordination networks containing various irregular cavities and channels, namely $[Ag_4(L^1)_2(NO_3)_4]\cdot H_2O$ (**1**), $[Ag(L^1)](BF_4)\cdot 2H_2O$ (**2**) and $[Ag_2(L^1)(H_2O)](ClO_4)_2$ (**3**). The present work not only suggests a significant role for counter ions but also illustrates the flexibility of the ligand in the construction of these frameworks. More interestingly, the coordination modes of the carboxylate groups in these silver(I) polymers show considerable diversity, and the novel rhombic tetrameric Ag_4O_2 subunit and μ_3-η^1 coordination mode of the carboxylate group in complex **1** are found in silver(I) carboxylates for the first time.



1,3-bis(pyridinio-4-carboxylato)-propane, L^1

Experimental

General

All chemicals were commercially available and used as received. The FT-IR spectra were recorded on a Nicolet Magna 750 using KBr pellets. The C, H, and N microanalyses were performed in the Element Analysis Laboratory of our institute.

CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Syntheses

$[Ag_4(L^1)_2(NO_3)_4]\cdot H_2O$ 1. An aqueous solution (8 mL) containing $AgNO_3$ (0.34 g, 2 mmol) and L^1 [10] (0.29 g, 1 mmol) was stirred at about 60 °C for a few minutes and then filtered. The filtrate was kept at room temperature for several weeks to give colorless polyhedral crystals of **1** (*ca.* 63% yield based on L^1).

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† Electronic supplementary information (ESI) available: perspective views of the packed structures of 1–3. See http://www.rsc.org/suppdata/dt/b1/b109298g/

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Table 1 Crystallographic data for complexes **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{30}H_{30}Ag_4N_8O_{21}$	$C_{15}H_{18}AgBF_4N_2O_6$	$C_{15}H_{16}Ag_2Cl_2N_2O_{13}$
Formula weight	1270.10	516.99	718.94
Crystal system	Triclinic	Monoclinic	Monoclinic
Crystal size/mm	0.52 × 0.36 × 0.09	0.65 × 0.43 × 0.41	0.56 × 0.40 × 0.32
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	7.8928(5)	5.7779(2)	5.7755(3)
b/Å	9.8427(7)	12.8758(4)	30.745(1)
c/Å	12.4498(8)	25.7377(7)	12.1968(5)
α/°	81.651(1)		
β/°	80.424(1)	90.487(1)	92.125(1)
γ/°	88.667(1)		
V/Å^3	943.6(1)	1914.7(1)	2164.3(2)
Z	1	4	4
F(000)	622	1032	1408
ρ_{calc}/g cm^{-3}	2.235	1.793	2.206
T/K	293(2)	293(2)	293(2)
μ/mm^{-1}	2.145	1.126	2.129
θ range/°	1.68 to 25.03	1.77 to 25.07	1.32 to 25.04
h, k, l range	$-8 \le h \le 9$	$-6 \le h \le 6$	$-2 \le h \le 6$
	$-11 \le k \le 9$	$-12 \le k \le 15$	$-32 \le k \le 36$
	$-14 \le l \le 14$	$-30 \le l \le 12$	$-14 \le l \le 14$
Data collected	4750	5630	7323
Unique data (R_{int})	3248 (0.0252)	3329 (0.0312)	3809 (0.0199)
Observed data [$I > 2\sigma(I)$]	2733	2720	3308
No. of parameters	285	261	308
Maximum/minimum effective transmission	0.8683/0.3869	1.0000/0.4658	1.0000/0.8352
R_1, wR_2 [$I > 2\sigma(I)$]^{a}, ^{b}	0.0449, 0.1206	0.0552, 0.1402	0.0566, 0.1421
Largest difference peak and hole/e Å^{-3}	0.927 and −1.776	0.926 and −0.776	2.065 and −2.555 (close to Ag atom)

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w^{-1} = \sigma^2(F^2_o) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$, where $a = 0.0846$ and $b = 0.0$ for **1**, $a = 0.0711$ and $b = 4.9435$ for **2**, $a = 0.0628$ and $b = 12.3925$ for **3**.

Calc. for $C_{30}H_{30}Ag_4N_8O_{21}$ **1**: C, 28.37; H, 2.38; N, 8.82. Found: C, 27.85; H, 2.21; N, 8.54%. IR (KBr, cm^{-1}): 3456 brs, 3115 m, 3049 m, 3001 m, 2949 m, 2426 w, 2395 w, 1763 w, 1686 w, 1643 s, 1610 s, 1564 s, 1462 m, 1433 m, 1385 s, 1360 s, 1352 s, 1325 m, 1277 w, 1207 w, 1174 m, 1130 w, 1109 w, 1070 w, 1041 w, 1001 w, 889 w, 850 w, 823 m, 781 m, 769 w, 746 w, 685 m, 661 w, 602 w, 486 w.

[Ag(L^1)](BF$_4$)·2H$_2$O 2. This complex was prepared by the procedure described for **1** using $AgBF_4$ instead of $AgNO_3$. A colorless crystalline solid of **2** was obtained (*ca.* 55% yield based on L^1). Calc. for $C_{15}H_{18}AgBF_4N_2O_6$ **2**: C, 34.85; H, 3.51; N, 5.42. Found: C, 34.24; H, 3.36; N, 5.27%. IR (KBr, cm^{-1}): 3440 brs, 3113 s, 3049 s, 3034 s, 2987 m, 2949 m, 2814 w, 1984 w, 1689 m, 1643 s, 1610 s, 1564 s, 1462 s, 1441 m, 1387 s, 1360 s, 1352 s, 1325 m, 1227 m, 1207 m, 1174 s, 1070 s, 1036 s, 1001 m, 889 m, 850 m, 823 s, 781 s, 769 m, 744 m, 685 s, 661 m, 602 s, 532 s, 521 m, 488 m, 424 m.

[Ag$_2$(L^1)(H$_2$O)](ClO$_4$)$_2$ 3. This complex was prepared by the procedure described for **1** using $AgClO_4$ instead of $AgNO_3$. A colorless crystalline solid of **3** was obtained (*ca.* 70% yield based on L^1). Calc. for $C_{15}H_{16}Ag_2Cl_2N_2O_{13}$ **3**: C, 25.06; H, 2.21; N, 3.90. Found: C, 24.87; H, 2.16; N, 3.77%. IR (KBr, cm^{-1}): 3442 brs, 3115 m, 3049 m, 2951 w, 1637 s, 1614 s, 1564 s, 1458 m, 1367 s, 1279 w, 1248 w, 1215 w, 1111 s, 1082 s, 879 w, 854 w, 823 w, 783 m, 700 m, 685 m, 661 w, 625 s, 472 w.

Crystallography

The crystallographic data for complexes **1**–**3** are summarized in Table 1. The X-ray diffraction measurements for the three complexes were performed on a Siemens SMART CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Intensity data were collected in the ω-scan mode. Lorentz polarization and absorption corrections were applied.[11] The structures were solved by direct methods and refined by full-matrix least-squares calculations using the SHELXTL-PC program[12,13] and anisotropic thermal parameters for all non-hydrogen atoms except the disordered atoms. The fluorine atoms of the discrete tetrafluoroborate groups in complex **2** display disorder, each having a site occupancy factor of 0.5. The hydrogen atoms on carbon atoms were generated geometrically, while the aqua hydrogen atoms were not located.

CCDC reference numbers 165476–165478.

See http://www.rsc.org/suppdata/dt/b1/b109298g/ for crystallographic data in CIF or other electronic format.

Results and discussion

Although compounds **2** and **3** were synthesized by the same procedure as that of compound **1** using $AgBF_4$ and $AgClO_4$, respectively, instead of $AgNO_3$, the resulting products differ in regard to their silver(I)/L^1 ratios and molecular structures, which may arise from the different coordinating ability of NO_3^-, BF_4^- and ClO_4^-, and the effects of anionic templates may dictate their adopted crystal structures.

X-Ray structure determination has revealed that complex **1** has a two-dimensional open network composed of a rhombic tetrameric subunit as shown in Fig. 1. Selected bonds distances and angles are given in Table 2. The centrosymmetric subunit is made up of four Ag atoms bridged by two O atoms from two different carboxylate groups in μ_3-η^1 coordination mode to form a novel Ag_4O_2 distorted octahedral conformation. There are two types of silver environments. The coordination geometry around the Ag(1) atom can be described as a distorted trigonal bipyramid with two μ_3-carboxylates and two nitrate ligands. The Ag(1)–O distances for the μ_3-carboxylate groups are 2.484(4) and 2.449(4) Å. Each Ag(1) atom also makes two intermediate contacts (2.531(5) and 2.622(6) Å) with the oxygen atoms of a bidentate chelating nitrate and one strong bond (2.412(6) Å) to a monodentate nitrate. The Ag(2) atom is coordinated by three carboxylate oxygen atoms in a T-shaped environment (O(4C)–Ag(2)–O(1) 93.3(2), O(3B)–Ag(2)–O(1) 106.1(1)°). The Ag(2)–O distances for the bidentate carboxylate groups are 2.188(4) and 2.180(4) Å, which are significantly

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Ag(1)–O(8)	2.412(6)	Ag(2)–O(3B)	2.180(4)
Ag(1)–O(1A)	2.449(4)	Ag(2)–O(4C)	2.188(4)
Ag(1)–O(1)	2.484(4)	Ag(2)–O(1)	2.489(4)
Ag(1)–O(5)	2.531(5)	Ag(1) ··· Ag(2A)	3.2344(7)
Ag(1)–O(6)	2.622(6)	Ag(2) ··· Ag(2D)	2.8473(8)
O(8)–Ag(1)–O(1A)	106.1(2)	O(6)–Ag(1) ··· Ag(2A)	87.7(1)
O(8)–Ag(1)–O(1)	164.3(1)	O(3B)–Ag(2)–O(4C)	160.4(2)
O(1A)–Ag(1)–O(1)	72.1(2)	O(3B)–Ag(2)–O(1)	106.1(1)
O(8)–Ag(1)–O(5)	96.8(2)	O(4C)–Ag(2)–O(1)	93.3(2)
O(1A)–Ag(1)–O(5)	155.7(2)	O(3B)–Ag(2)–Ag(2D)	83.2(1)
O(1)–Ag(1)–O(5)	83.7(1)	O(4C)–Ag(2) ··· Ag(2D)	80.0(1)
O(8)–Ag(1)–O(6)	90.5(2)	O(1)–Ag(2) ··· Ag(2D)	156.3(1)
O(1A)–Ag(1)–O(6)	136.8(2)	O(3B)–Ag(2) ··· Ag(1A)	69.0(1)
O(1)–Ag(1)–O(6)	101.3(2)	O(4C)–Ag(2) ··· Ag(1A)	128.8(1)
O(5)–Ag(1)–O(6)	48.8(2)	O(1)–Ag(2) ··· Ag(1A)	48.6(1)
O(8)–Ag(1) ··· Ag(2A)	106.5(1)	Ag(2D) ··· Ag(2) ··· Ag(1A)	119.95(3)
O(1A)–Ag(1) ··· Ag(2A)	49.63(9)	Ag(1A)–O(1)–Ag(1)	107.9(2)
O(1)–Ag(1) ··· Ag(2A)	84.5(1)	Ag(1A)–O(1)–Ag(2)	81.8(1)
O(5)–Ag(1) ··· Ag(2A)	131.0(1)	Ag(1)–O(1)–Ag(2)	100.3(1)

Symmetry transformations used to generate equivalent atoms: A: $-x + 3, -y + 2, -z + 3$; B: $x + 1, y, z + 1$; C: $-x + 3, -y + 2, -z + 2$; D: $-x + 4, -y + 2, -z + 3$.

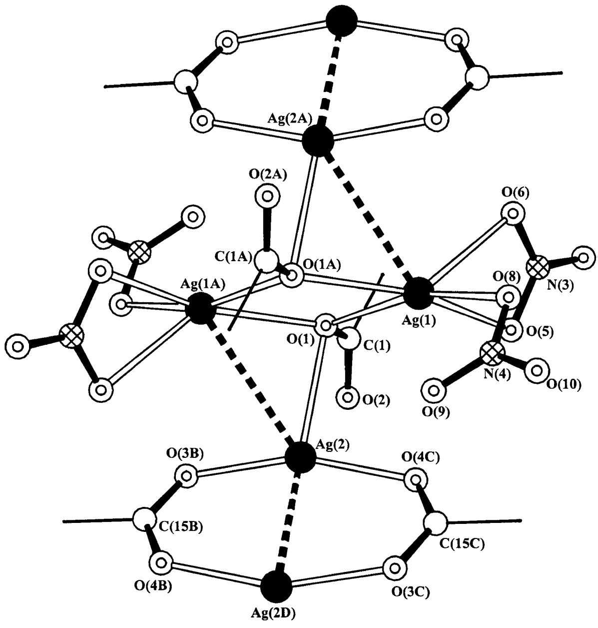


Fig. 1 The Ag_4O_2 subunit showing the local coordination environments of Ag(I) ions in complex **1**. Only the Ag, O, α-carbon atoms and nitrate groups are shown.

shorter than that for the μ_3-carboxylate groups (2.489(4) Å). The tetrameric Ag_4O_2 subunits are extended into infinite chains in the *a* direction through the linkage of two different Ag(2) atoms of adjacent subunits, which are doubly bridged by *syn–syn* μ-*O*,*O*′ groups of carboxylate ligands (Fig. 2). In comparison with the Ag ··· Ag separation (2.89 Å) in metallic silver,[14] the Ag(2) ··· Ag(2D) distance of 2.8473(8) Å is thus suggestive of a stronger metal–metal interaction. Nevertheless, there also exists a weak interaction between the Ag(1) and Ag(2A) atoms with a separation of 3.2344(7) Å. The two carboxylate groups in the same L^1 ligand adopt different coordination modes: one is μ_3-η^1 and the other bridging bidentate. Adjacent chains are cross-linked by L^1 in an end-to-end mode leading to a 2-D open network parallel to the *ac* plane, which contains rhombic cavities (*ca.* 9 × 7 Å). The stacking of the layers gives extended channels, directed along the *b* direction, in which the lattice water molecules are accommodated.

The structure of complex **2** is based on a two-dimensional cationic polymeric layer containing bis(carboxylate-*O*,*O*′)-bridged centrosymmetric dimeric subunits (Fig. 3). Table 3 gives the selected bond distances and angles. The Ag ··· Ag separation (2.8728(9) Å) in the dimeric subunit, in which each pair of silver(I) atoms is doubly bridged by coplanar *syn–syn* μ-carboxylato-*O*,*O*′ groups, is close to that in metallic silver and hence indicative of a comparable metal–metal interaction. The intra-dimer Ag–O distances (2.220(4), 2.224(4) Å) and

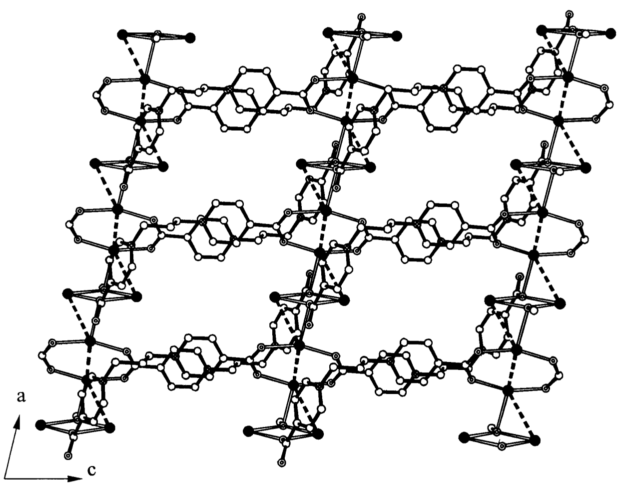


Fig. 2 Perspective view of complex **1** showing the 2-D layer parallel to the *ac* plane. Hydrogen atoms, nitrate groups and lattice water molecules have been omitted for clarity.

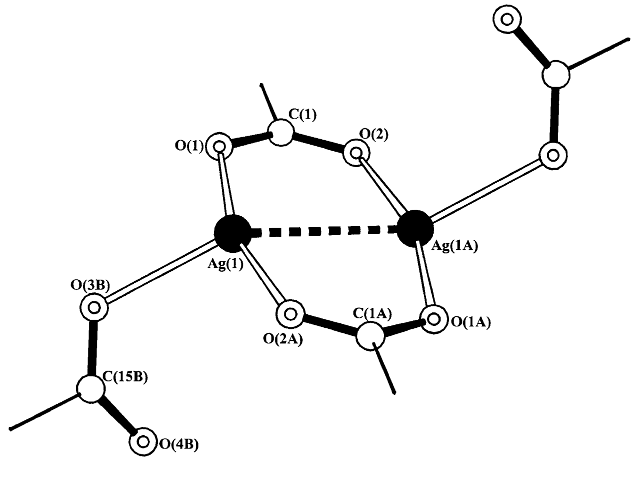


Fig. 3 The dimeric subunits showing the local coordination environments of Ag(I) ions in complex **2**. Only the Ag, O and α-carbon atoms are shown.

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Ag(1)–O(2A)	2.220(4)	O(2)–Ag(1A)	2.220(4)
Ag(1)–O(1)	2.224(4)	Ag(1) ··· Ag(1A)	2.8728(9)
Ag(1)–O(3B)	2.396(5)		
O(2A)–Ag(1)–O(1)	162.6(2)	O(2A)–Ag(1) ··· Ag(1A)	79.1(1)
O(2A)–Ag(1)–O(3B)	97.5(2)	O(1)–Ag(1) ··· Ag(1A)	83.9(1)
O(1)–Ag(1)–O(3B)	99.1(2)	O(3B)–Ag(1) ··· Ag(1A)	149.1(1)

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

O–Ag–O angle (162.6(2)°) are comparable to those found in the dimeric structures of known silver(I) betaine complexes.[8] The axial positions of the dimer are occupied by the oxygen atoms from the carboxylate groups of symmetry-related ligands in a monodentate coordination mode (Ag(1)–O(3B) 2.396(5) Å). Accordingly, the silver(I) atoms in the dimer are coordinated in a T-shaped environment (O(2A)–Ag(1)–O(3B) 97.5(2), O(1)–Ag(1)–O(3B) 99.1(2)°). A perspective view of complex **2** is shown in Fig. 4. The carboxylate groups of each L^1 ligand show two coordination modes: common *syn–syn* bridging bidentate and monodentate. The [Ag_2(carboxylate-*O*,*O′*)$_2$] dimers are bridged by the double betaine ligands in an end-to-end mode to form a two-dimensional open framework along the *bc* plane, which contains a large disordered rhombus (64-membered rings) with a silver(I) atom at each corner and an L^1 ligand at each edge connecting two silver(I) atoms. The metal–metal distances through the bridging L^1 are 13.7 and 13.9 Å. Similar to complex **1**, the networks of **2** stack in a parallel fashion without interpenetration to generate large channels along the *a* direction, which are occupied by the discrete BF_4^- ions and lattice water molecules.

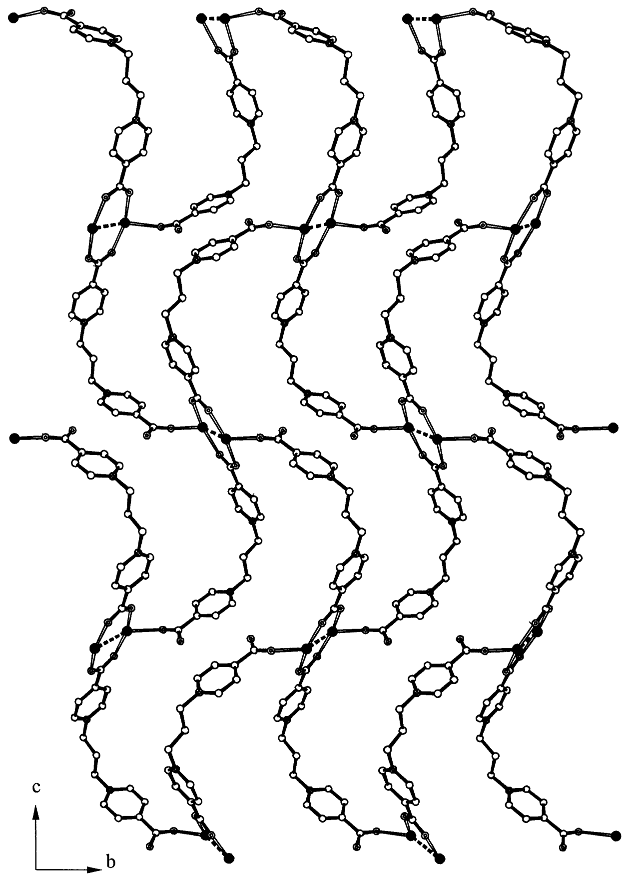


Fig. 4 Perspective view of complex **2** showing the 2-D layer corresponding to the *bc* plane. Hydrogen atoms, BF_4^- ions and lattice water molecules have been omitted for clarity.

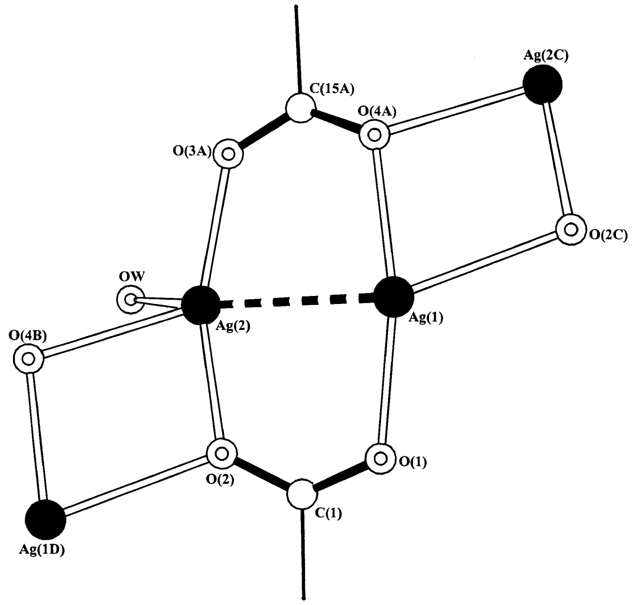


Fig. 5 The dimeric subunits showing the local coordination environments of Ag(I) ions in complex **3**. Only the Ag, O and α-carbon atoms are shown.

The structure of complex **3** comprises a two-dimensional cationic network built from bis(carboxylate-*O*,*O′*)-bridged dimeric subunits (Fig. 5). Table 4 lists the selected bond distances and angles. There are two crystallographically independent silver(I) atoms in this complex. The intra-dimer Ag ··· Ag separation (2.992(1) Å) is slightly longer than that in metallic silver and suggestive of a comparable but weaker metal–metal interaction. The intra-dimer Ag–O distances (2.239(4), 2.281(4) Å for Ag(1); 2.192(5), 2.247(4) Å for Ag(2)) and O–Ag–O angles (166.2(2) for Ag(1), 149.5(2)° for Ag(2)) are comparable to those in complex **2**. The axial positions of the dimer are occupied by two carboxylate oxygen atoms (Ag(1)–O(2C) 2.621(5), Ag(2)–O(4B) 2.573(5) Å). The Ag(1) atom is coordinated by three carboxylate oxygen atoms in a T-shaped environment (O(4A)–Ag(1)–O(2C) 75.47(16), O(1)–Ag(1)–O(2C) 115.6(2)°). However, the coordination sphere of the Ag(2) atom is completed by an additional aqua ligand (Ag(2)–OW 2.57(1) Å), making the stereochemistry about the silver atom a strongly distorted tetrahedron (77.0(2)–149.5(2)°). Each carboxylate group in this complex coordinates in a tridentate mode, and each pair of adjacent metal atoms are bonded by two kinds of carboxylate bridges, forming a [Ag_2(carboxylate-*O*,*O′*)$_2$] eight-membered ring and a rhombic Ag_2O_2 unit. The dimeric subunits are extended into a step polymeric chain in the *a* direction through the linkage of each metal centre to the carboxylate groups of an adjacent dimer (Fig. 6a). Such chains are further cross-linked by the molecular skeletons of the flexible double betaine ligands, thereby extending the structure into a plane wave-like layer along the *ab* plane with distorted rectangular pores (*ca.* 14.7 × 5.8 Å). The crystal structure is built up from a non-interpenetrating packing of these sheets such that the shortest Ag ··· Ag distance between adjacent layers is 3.319(1) Å (Fig. 6b). The perchlorate groups, having no contact with the metal ions, reside in the resultant channels.

Table 4 Selected bond lengths (Å) and angles (°) for complex **3**

Ag(1)–O(1)	2.239(4)	Ag(2)–O(2)	2.247(4)
Ag(1)–O(4A)	2.281(4)	Ag(2)–OW	2.57(1)
Ag(1)–O(2C)	2.621(5)	Ag(2)–O(4B)	2.573(5)
Ag(2)–O(3A)	2.192(5)	Ag(1) ··· Ag(2)	2.992(1)
O(1)–Ag(1)–O(4A)	166.2(2)	O(2)–Ag(2)–OW	114.7(3)
O(1)–Ag(1)–O(2C)	115.6(2)	O(3A)–Ag(2)–O(4B)	116.4(2)
O(4A)–Ag(1)–O(2C)	75.5(2)	O(2)–Ag(2)–O(4B)	77.0(2)
O(1)–Ag(1) ··· Ag(2)	83.1(1)	OW–Ag(2)–O(4B)	78.1(3)
O(4A)–Ag(1) ··· Ag(2)	83.3(1)	O(3A)–Ag(2) ··· Ag(1)	76.9(1)
O(2C)–Ag(1) ··· Ag(2)	147.7(1)	O(2)–Ag(2) ··· Ag(1)	76.1(1)
O(3A)–Ag(2)–O(2)	149.5(2)	OW–Ag(2) ··· Ag(1)	141.9(3)
O(3A)–Ag(2)–OW	95.4(4)	O(4B)–Ag(2) ··· Ag(1)	138.9(1)

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

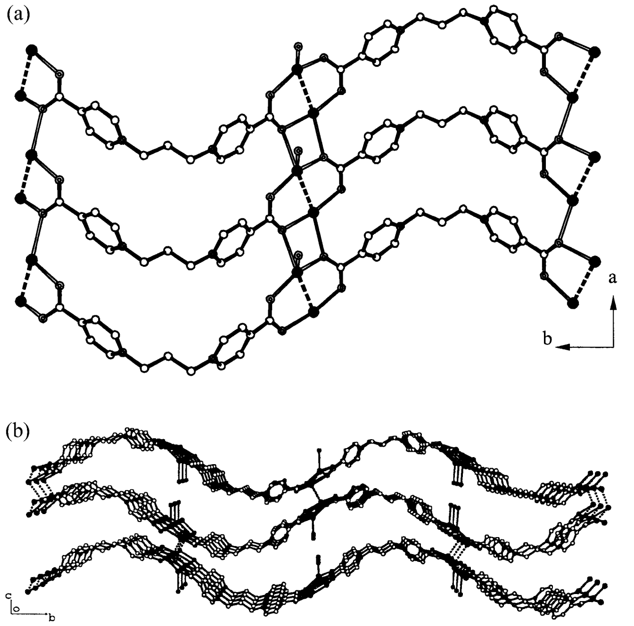
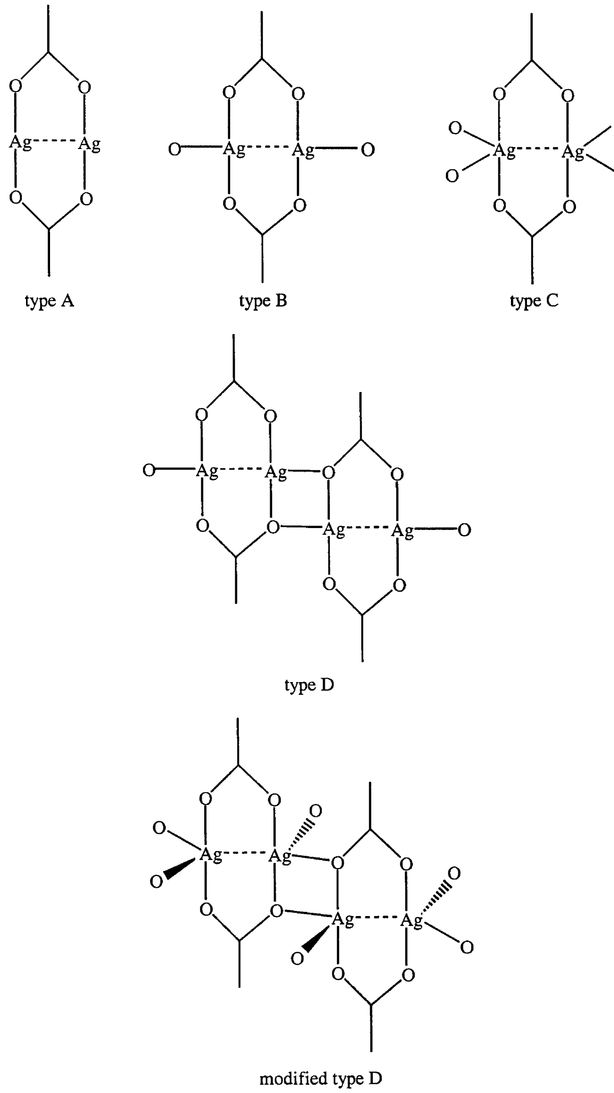


Fig. 6 Perspective view of complex **3** showing (a) the 2-D layer corresponding to the *ab* plane and (b) the packing drawing of the 2-D layers viewed along the *a* direction. Hydrogen atoms and perchlorate groups have been omitted for clarity.

The coordination chemistry of silver(I) carboxylates has been extensively investigated. Among the characterized crystal structures of silver(I) carboxylates, most are composed of either discrete dimers or polymeric systems constructed through the linkage of dimeric subunits. Each pair of adjacent metal atoms is doubly bridged by coplanar *syn–syn* μ-*O*,*O′* carboxylate ligands, which have been classified into four principal types (Scheme 1).[8] Type **A** contains discrete [Ag$_2$(carboxylate-*O*,*O′*)$_2$] dimers without any axial ligand. **B** and **C** have similar dimeric structures with the axial site(s) occupied by one and two ligands, respectively, usually leading to polymeric species. **D** comprises dimeric subunits that extend into a step polymer through the linkage of each metal centre to the carboxylate groups of an adjacent dimer, whereas modified type **D** has an additional axial ligand attached to each metal atom. The dimer in complex **2** belongs to type **B**. Complex **3** possesses dimeric subunits similar to those of modified type **D**, but only one metal centre of the dimer bears an additional axial ligand. It is noteworthy that the polymeric structure of complex **1**, which is based on the unprecedented rhombic tetrameric subunit, is distinct from the known silver(I) carboxylates. Moreover, to our knowledge, the μ_3-η^1 coordination mode of the carboxylate group in complex **1** is found for the first time among the silver(I) carboxylates. Therefore, complex **1** is unique among silver(I) carboxylate complexes and constitutes a new structural variety in metal carboxylate chemistry.



Scheme 1 Dimer structures in silver(I) carboxylate complexes.

It is noted that in comparison with the Ag ··· Ag separation (2.89 Å) in metallic silver and twice the covalent radius of silver (1.33 and 1.455 Å for two- and four-coordinate silver, respectively),[15] the Ag ··· Ag separation in the present compounds provides supporting evidence for the significance of *argentophilicity*,[16] which is a complementary logical extension of the well-established concept of aurophilicity for gold(I) complexes.[17]

Conclusion

Three novel 2-D coordination polymers with open layer structures were prepared from the self-assembly reactions of a new flexible double betaine, L^1, with silver(I) salts. The variation of the anions of the silver salts in the synthetic procedure results in different structural frameworks, subunits, coordination modes of the carboxylate groups and geometries of the silver(I) atoms. In complexes **1**–**3**, the 2-D open networks stack in a parallel fashion to create channels of various sizes and shapes with a neutral framework in **1** and positively-charged frameworks in **2** and **3**. This work demonstrates the feasibility of achieving novel cavities or channels in polymeric frameworks by the self-assembly of flexible double betaines and metal ions. Further studies will aim at the syntheses of new flexible double betaines and other multifunctional ligands with a long flexible chain skeleton, as well as their application in crystal engineering.

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