Building Two-dimensional Silver(I) Co-ordination Polymers with Dicarboxylate-like Ligands: Synthesis and Crystal Structures of Polymeric Complexes of Silver Nitrate and Perchlorate with Flexible Double Betaines†

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Four novel two-dimensional silver(I) co-ordination polymers of two flexible double betaines with different quaternary ammonio side groups in the adipic acid skeleton, namely $[\{Ag_2(L^1)\}_n][ClO_4]_{2n}$ **1**, $[\{Ag_2(L^2)\}_n][ClO_4]_{2n}\cdot 2nH_2O$ **2**, $[\{Ag_2(L^1)(NO_3)_2\}_n]$ **3** and $[\{Ag_2(L^2)(NO_3)_2\}_n]$ **4** [L^1 = *meso*-2,5-bis(trimethylammonio)adipate, $^-O_2CCH(N^+Me_3)CH_2CH_2CH(N^+Me_3)CO_2^-$; L^2 = *meso*-2,5-bis(pyridinio)adipate, $^-O_2CCH(N^+C_5H_5)CH_2CH_2CH(N^+C_5H_5)CO_2^-$], have been prepared and characterized by X-ray crystallography. Each complex contains dimeric subunits in which each pair of adjacent metal atoms is doubly bridged by coplanar *syn-syn* μ-carboxylato-*O,O′* groups. The dimeric subunits are extended into a step polymer through the linkage of each metal centre to a carboxylate group of an adjacent dimer. Such $[Ag_2(\text{carboxylate-}O,O')_2]_n$ chains are extended into sawtooth-wave layer structures in **1**, **3** and **4**, and an unusual corrugated layer in **2** by the cross-linkage of the adipic acid skeleton of the double-betaine ligands. The different ligation ability of the perchlorate and nitrate anions results in different co-ordination geometries about the silver(I) atoms. In **1** and **2**, the silver(I) atom is co-ordinated by three carboxylato oxygen atoms in a T-shaped geometry, and the $[Ag_2(\text{carboxylate-}O,O')_2]_n$ chain exhibits the typical type D structure. The co-ordination geometry of the silver(I) atom in **3** is a distorted tetrahedron, and the $[Ag_2(\text{carboxylate-}O,O')_2]_n$ chain adopts a modified type D structure. The silver(I) atom in **4** exhibits unusual five-co-ordination in a square pyramid, and the dimer is converted into a novel paddlewheel-like structure, which is the first example found in silver(I) carboxylates.

Transition-metal co-ordination polymers of one-, two- and three-dimensional infinite frameworks have been the subject of intensive research for several decades, and major advances have been made in both their theoretical description and application as new materials.[1] The chemistry of metal co-ordination polymers is among the most promising interfaces between synthetic chemistry and material science, as it provides a solid foundation for understanding how molecules can be organized and how functions can be achieved. Thus the structural design or modification of the framework has become a very active field in crystal engineering.

In our research program, we plan to study the formation of co-ordination polymers of silver(I) complexes using various dicarboxylate-like ligands. Silver(I) principally exhibits linear, trigonal and tetrahedral co-ordination,[2,3] and frequently forms either discrete dimers or polymeric systems constructed by the linkage of dimeric sub-units in which each pair of adjacent metal atoms is doubly bridged by coplanar *syn-syn* μ-O,O′ groups of carboxylate ligands. These dimeric structures, formulated as $[Ag_2(\text{carboxylato-}O,O')_2]_n$ (n = 1 or ∞), have been classified into four types (Fig. 1).[4–13] Type A complexes form discrete dimers, types B and C have additional oxygens in the terminal positions of the dimer, while in type D dimers the terminal oxygens extend the structure into a polymer through adjacent carboxyl groups. As expected, new step polymers in which the co-ordinated metal atoms constitute a part of the backbone can be formed by using dicarboxylate ligands to cross-link such dimeric subunits.

Our previous studies have demonstrated that betaine ($Me_3N^+CH_2CO_2^-$, IUPAC name: trimethylammonioacetate) and its derivatives, considered as structural analogues of the corresponding carboxylate anions, can form stable silver(I) complexes which are soluble in water and ethanol.[14–19] We have recently obtained two-dimensional crystalline mercury(II) chloride adducts[20] and co-ordination polymers of sodium perchlorate with layer, double-layer or three-dimensional networks[21] by using a series of three flexible double betaines with different polymethylene bridges between the quaternary nitrogen atoms.[22] In the present work, we report the preparation and characterization of four new silver(I) dicarboxylate-like complexes containing two-dimensional frameworks constructed from two flexible double betaines with different quaternary ammonio side groups in the adipic acid skeleton, namely $[\{Ag_2(L^1)\}_n][ClO_4]_{2n}$ **1**, $[\{Ag_2(L^2)\}_n][ClO_4]_{2n}\cdot 2nH_2O$ **2**, $[\{Ag_2(L^1)(NO_3)_2\}_n]$ **3** and $[\{Ag_2(L^2)(NO_3)_2\}_n]$ **4** [L^1 = *meso*-2,5-bis(trimethylammonio)adipate, $^-O_2CCH(N^+Me_3)CH_2CH_2CH(N^+Me_3)CO_2^-$; L^2 = *meso*-2,5-bis(pyridinio)adipate, $^-O_2CCH(N^+C_5H_5)CH_2CH_2CH(N^+C_5H_5)CO_2^-$].

Experimental

Materials and Measurements.—*meso*-2,5-Dibromoadipic acid was purchased from Sigma, and other reagents from BDH. Proton NMR data were determined using a Bruker WM250 NMR spectrometer. Infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Perkin-Elmer 1600 FT-IR spectrometer.

Preparations.—meso-*2,5-Bis(trimethylammonio)adipate* (L^1). A solution of *meso*-2,5-dibromoadipic acid (5.05 g, 15.8 mmol) in aqueous trimethylamine (50 cm^3, 45%) was stirred at

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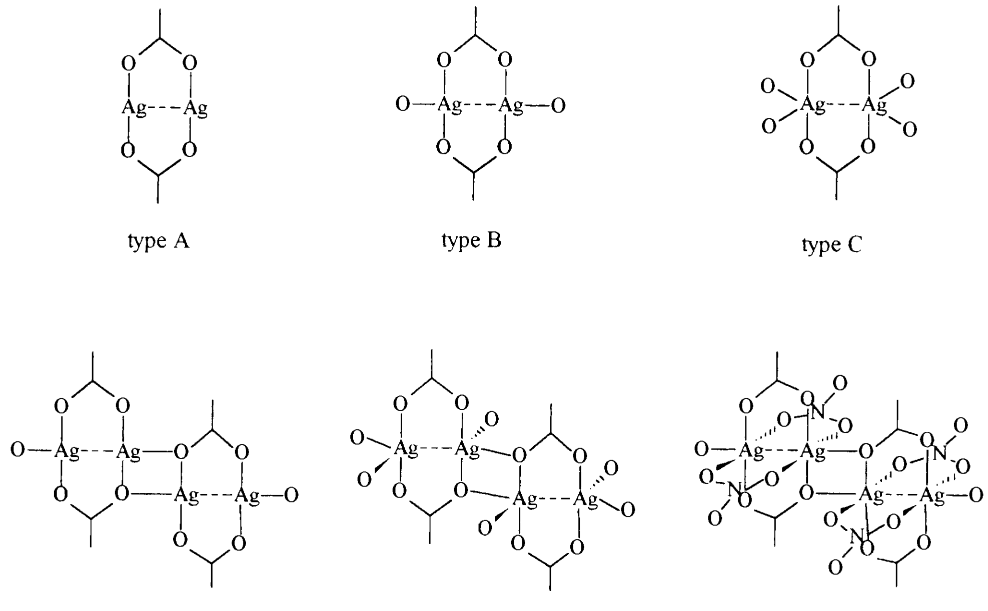
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



type A type B type C

type D modified type D paddlewheel-like structure

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

Table 1 Data collection and processing parameters for complexes **1**–**4**

Complex	**1**	**2**	**3**	**4**
Formula	$C_{12}H_{24}Ag_2Cl_2N_2O_{12}$	$C_{16}H_{20}Ag_2Cl_2N_2O_{14}$	$C_{12}H_{24}Ag_2N_4O_{10}$	$C_{16}H_{16}Ag_2N_4O_{10}$
M	675.0	751.0	600.1	640.1
Colour, habit	Colourless needle	Colourless block	Colourless needle	Colourless polyhedron
Crystal size/mm	0.12 × 0.20 × 0.25	0.10 × 0.18 × 0.20	0.12 × 0.20 × 0.35	0.20 × 0.20 × 0.25
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	5.833(7)	5.460(3)	8.170(3)	5.396(2)
b/Å	8.330(5)	13.835(2)	5.710(2)	8.906(4)
c/Å	20.963(6)	15.824(9)	20.845(9)	10.922(6)
α/°	90	84.28(4)	90	66.93(4)
β/°	94.53(6)	81.79(4)	91.38(2)	81.89(4)
γ/°	90	86.92(4)	90	84.33(4)
U/Å^3	1013.5(13)	1176.2(6)	972.1(9)	477.5(4)
Z	2	2	2	1
$F(000)$	668	740	596	314
D_c/g cm^{-3}	2.212	2.120	2.050	2.226
μ/mm^{-1}	2.26	1.97	2.07	2.12
Transmission factors	0.903–1.000	0.810–1.000	0.649–0.849	0.975–1.000
Collection range; $2\theta_{max}$	$h, k, \pm l$; 52°	$\pm h, -k, \pm l$; 52°	$h, -k, \pm l$; 50°	$\pm h, -k, \pm l$; 52°
Unique data measured	1998	4616	1538	1886
Observed data [$F \geqslant 4\sigma(F)$], n	1698	3659	1349	1831
No. of variables, p	133	308	128	146
R	0.060	0.054	0.035	0.028
R'	0.086	0.078	0.044	0.036
S (Goodness of fit)	2.51	2.58	1.07	2.48
Residual extremes in final difference map/e Å^{-3}	+1.86, −1.26	+1.45, −0.93	+0.74, −1.20	+0.82, −1.16

$R = \Sigma\Delta/\Sigma|F_o|$, $R' = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ and $S = [\Sigma w\Delta^2/(n - p)]^{\frac{1}{2}}$ where $w = [\sigma^2(F_o) + K|F_o|^2]^{-1}$ and $\Delta = ||F_o| - |F_c||$; 10^4K = 5, 3, 8 and 0.5 for complexes **1**, **2**, **3** and **4**, respectively.

room temperature overnight. The white powdery residue obtained after evaporation of excess aqueous trimethylamine at *ca.* 70 °C under reduced pressure was loaded in an Amberlite IR-400 anionic exchange column (resin in hydroxide form) and eluted with distilled water. Removal of water by a rotary evaporator under reduced pressure and trituration with acetone afforded a white powdery product (3.63 g, 88% yield). Proton NMR data (CD_3OD, $SiMe_4$ as internal standard): δ 1.95 (4 H, t, CH_2), 3.32 (18 H, m, CH_3) and 3.61 (2 H, m, CH).

meso-2,5-*Bis(pyridinio)adipate* (L^2). This compound was synthesized in a similar manner. The *meso*-2,5-dibromoadipic acid (5.03 g, 15.7 mmol) was mixed with pyridine (30 cm^3) and distilled water (20 cm^3). The resulting solution was stirred at room temperature overnight. After removal of pyridine and distilled water by a rotary evaporator under reduced pressure, a yellowish powder was obtained, which was passed through an Amberlite IR-400 anionic exchange column resin (OH^- form), and the elute was then dehydrated to yield a yellowish solid. Trituration with ethanol gave a white powdery product (3.42 g, 73% yield). Proton NMR data (D_2O, H_2O as internal

Table 2 Atomic coordinates (× 10^5 for Ag, × 10^4 for others) for complexes **1–4**

Atom	x	y	z	Atom	x	y	z
$[\{Ag_2(L^1)\}_n][ClO_4]_{2n}$ **1**							
Ag(1)	29 060(9)	−7 458(7)	51 086(3)	Cl(1)	5 706(3)	1 484(2)	6 525(1)
O(1)	1 173(8)	1 550(6)	4 742(2)	O(3)	5 238(26)	2 420(16)	7 075(5)
O(2)	4 532(8)	2 596(6)	4 510(2)	O(4)	5 786(21)	2 467(13)	5 980(4)
N(1)	257(9)	3 864(7)	3 538(2)	O(5)	4 065(26)	256(18)	6 452(9)
C(1)	2 405(11)	2 615(8)	4 519(3)	O(6)	7 927(18)	764(18)	6 643(8)
C(2)	1 218(11)	4 148(8)	4 238(3)	O(3′)	5 711(25)	2 706(14)	6 994(5)
C(3)	−558(12)	4 833(10)	4 666(3)	O(4′)	7 111(32)	1 941(23)	6 032(8)
C(4)	2 201(12)	3 576(12)	3 126(4)	O(5′)	3 429(18)	1 216(24)	6 232(8)
C(5)	−1 316(13)	2 446(10)	3 470(3)	O(6′)	6 436(36)	−16(15)	6 775(9)
C(6)	−1 009(15)	5 326(11)	3 286(3)				
$[\{Ag_2(L^2)\}_n][ClO_4]_{2n}\cdot 2nH_2O$ **2**							
Ag(1)	30 461(10)	15 725(6)	68 804(3)	C(27)	11 403(17)	3 791(6)	3 912(5)
Ag(2)	68 829(9)	14 454(5)	78 852(3)	C(28)	11 487(14)	2 945(5)	4 447(5)
O(11)	1 058(8)	1 504(3)	8 213(3)	Cl(1)	4 926(4)	4 173(1)	8 110(1)
O(12)	4 024(8)	1 494(4)	9 040(3)	O(1)	6 337(34)	3 469(11)	7 679(12)
N(11)	−25(9)	2 249(3)	10 200(3)	O(2)	2 300(23)	4 017(12)	8 102(12)
C(11)	1 851(10)	1 472(4)	8 918(3)	O(3)	5 044(30)	5 124(8)	7 724(10)
C(12)	−124(11)	1 388(4)	9 718(3)	O(4)	4 840(32)	4 150(12)	9 036(8)
C(13)	251(11)	416(4)	10 248(4)	O(1′)	7 184(23)	3 571(10)	8 085(10)
C(14)	−1 615(14)	3 010(5)	10 048(5)	O(2′)	3 818(45)	3 835(17)	7 457(13)
C(15)	−1 550(17)	3 825(5)	10 450(5)	O(3′)	5 672(37)	5 134(10)	7 977(13)
C(16)	180(16)	3 915(5)	10 977(5)	O(4′)	3 574(25)	3 914(10)	8 927(8)
C(17)	1 765(15)	3 151(5)	11 133(5)	Cl(2)	4 965(3)	−1 019(1)	7 557(1)
C(18)	1 667(12)	2 319(5)	10 724(4)	O(5)	6 742(26)	−480(10)	7 879(9)
O(21)	8 844(8)	1 406(4)	6 543(3)	O(6)	3 081(25)	−416(9)	7 207(9)
O(22)	5 896(8)	1 674(4)	5 715(3)	O(7)	6 249(30)	−1 506(12)	6 879(9)
N(21)	9 900(9)	2 254(3)	4 428(3)	O(8)	3 757(29)	−1 717(10)	8 174(9)
C(21)	8 070(10)	1 511(4)	5 849(3)	O(5′)	5 759(23)	−459(8)	8 159(7)
C(22)	10 027(11)	1 376(4)	5 053(3)	O(6′)	4 225(23)	−407(8)	6 861(7)
C(23)	9 697(12)	437(4)	4 687(4)	O(7′)	6 652(23)	−1 744(9)	7 202(9)
C(24)	8 236(12)	2 352(5)	3 877(4)	O(8′)	2 986(32)	−1 523(14)	8 053(13)
C(25)	8 105(15)	3 169(5)	3 331(5)	O(1W)	10 477(22)	3 548(9)	6 402(9)
C(26)	9 674(16)	3 905(5)	3 343(5)	O(2W)	15 181(25)	4 154(9)	5 543(9)
$[\{Ag_2(L^1)(NO_3)_2\}_n]$ **3**							
Ag(1)	−6 725(4)	20 664(7)	52 883(2)	C(4)	3 053(6)	1 942(9)	3 201(2)
O(1)	1 280(4)	3 531(6)	4 642(2)	C(5)	5 149(6)	4 930(9)	3 182(2)
O(2)	2 836(3)	318(6)	4 592(1)	C(6)	5 788(6)	1 110(10)	3 662(2)
N(1)	4 476(4)	2 954(7)	3 576(2)	N(2)	433(5)	3 686(10)	6 604(2)
C(1)	2 545(5)	2 447(8)	4 504(2)	O(3)	1 375(5)	3 173(10)	6 168(2)
C(2)	3 898(4)	3 978(8)	4 215(2)	O(4)	871(5)	4 975(12)	7 055(2)
C(3)	5 303(4)	4 334(8)		O(5)	−992(5)	2 923(7)	6 579(2)
$[\{Ag_2(L^2)(NO_3)_2\}_n]$ **4**							
Ag(1)	18 939(4)	57 079(3)	53 268(2)	C(5)	7 370(7)	3 460(5)	−279(3)
O(1)	4 002(4)	3 934(3)	4 269(3)	C(6)	5 617(7)	2 849(5)	−753(3)
O(2)	1 188(4)	3 200(3)	3 332(3)	C(7)	3 789(7)	1 878(4)	149(3)
N(1)	5 410(4)	2 189(3)	1 929(2)	C(8)	3 709(6)	1 558(4)	1 493(3)
C(1)	3 295(5)	3 145(3)	3 673(3)	N(2)	505(5)	1 811(3)	7 382(3)
C(2)	5 293(5)	1 919(3)	3 368(3)	O(3)	1 320(7)	3 094(3)	7 318(3)
C(3)	4 736(6)	166(4)	4 293(3)	O(4)	−803(6)	1 829(4)	6 534(3)
C(4)	7 223(6)	3 131(4)	1 061(3)	O(5)	957(6)	496(3)	8 300(3)

standard): δ 2.17 (4 H, m, CH_2), 5.12 (2 H, m, CH), 7.99 (4 H, *m*-H of pyridine), 8.48 (2 H, m, *p*-H of pyridine) and 8.75 (4 H, m, *o*-H of pyridine).

$[\{Ag_2(L^1)\}_n][ClO_4]_{2n}$ **1**. A solution of silver(I) perchlorate (212.6 mg, 1.0 mmol) in ethanol (5 cm^3) and a solution of L^1 (84.4 mg, 0.25 mmol) in ethanol (8 cm^3) were mixed to give a white precipitate, to which distilled water (20 cm^3) was added to obtain a clear colourless solution. The resulting solution was filtered and allowed to stand in a desiccator charged with Drierite for a week to give colourless needle crystals. IR: 3742.4s, 3675.4m, 3651.2m, 3027.5m, 2960.9m, 2936.7m, 2361.5s, 2337.3s, 2016.4w, 1865.1vw, 1616.8vs, 1471.5s, 1395.9s, 1371.7s, 1317.2m, 1286.9m, 1226.4w, 1087.1s, 960.0m, 893.4w, 851.0w, 802.6m, 742.0w, 681.5w, 627.0w and 470.8w cm^{-1}.

$[\{Ag_2(L^2)\}_n][ClO_4]_{2n}\cdot 2nH_2O$ **2**. To a mixture of silver(I) perchlorate (211.1 mg 1.0 mmol) and L^2 (82.3 mg, 0.25 mmol) was added water–ethanol (20 cm^3, 3 : 1 v/v). After stirring at *ca.* 60 °C for a few minutes, a clear solution was obtained. Storage of the solution in a desiccator charged with Drierite for a few days yielded colourless block-like crystals. IR: 3746.2m, 3669.2m, 3646.2m, 2361.5s, 2330.8s, 2200.0m, 2015.4m, 1838.5w, 1792.3vw, 1646.2s, 1561.5m, 1484.6s, 1361.5s, 1269.2w, 1161.5m, 1076.9m, 930.8w, 884.6vw, 853.8vw, 776.9w, 684.6vw, 607.7w and 476.9vw cm^{-1}.

$[\{Ag_2(L^1)(NO_3)_2\}_n]$ **3**. To silver(I) nitrate (170.1 mg, 1.0 mmol) dissolved in ethanol (3 cm^3), a solution of L^1 in water–ethanol (6 cm^3, 1 : 2 v/v) was added to give a white precipitate, which was dissolved by adding distilled water (10 cm^3). The resulting solution was filtered and allowed to stand in a

Table 3 Selected interatomic distances (Å) and angles (°) for complexes **1**–**4***

$[\{Ag_2(L^1)\}_n][ClO_4]_{2n}$ **1**

Ag(1)···Ag(1b)	2.810(1)	Ag(1)–O(1)	2.269(5)
Ag(1)–O(1d)	2.515(5)	Ag(1)–O(2b)	2.249(5)
C(1)–O(1)	1.255(8)	C(1)–O(2)	1.243(8)
C(1)–C(2)	1.547(9)		
Ag(1b)···Ag(1)–O(1)	86.7(1)	Ag(1b)···Ag(1)–O(1d)	168.9(1)
Ag(1b)···Ag(1)–O(2b)	78.4(1)	O(1)–Ag(1)–O(1d)	82.3(2)
O(1)–Ag(1)–O(2b)	164.5(2)	O(1d)–Ag(1)–O(2b)	112.5(2)
Ag(1)–O(1)–Ag(1d)	97.7(2)	C(1)–O(1)–Ag(1)	118.0(4)
C(1)–O(1)–Ag(1d)	144.1(4)	C(1)–O(2)–Ag(1b)	129.8(4)
O(1)–C(1)–O(2)	126.8(6)	O(1)–C(1)–C(2)	118.2(6)
O(2)–C(1)–C(2)	115.0(6)		

$[\{Ag_2(L^2)\}_n][ClO_4]_{2n}\cdot 2nH_2O$ **2**

Ag(1)···Ag(2)	2.794(1)	Ag(1)–O(11)	2.225(4)
Ag(1)–O(22)	2.234(4)	Ag(1)–O(21c)	2.456(5)
Ag(2)–O(12)	2.231(4)	Ag(2)–O(21)	2.243(4)
Ag(2)–O(11d)	2.416(4)	O(11)–C(11)	1.250(7)
O(12)–C(11)	1.231(7)	C(11)–C(12)	1.540(7)
O(21)–C(21)	1.225(7)	O(22)–C(21)	1.240(7)
C(21)–C(22)	1.551(7)		
Ag(2)···Ag(1)–O(11)	76.7(1)	Ag(2)···Ag(1)–O(22)	88.5(1)
Ag(2)···Ag(1)–O(21c)	157.2(1)	O(11)–Ag(1)–O(22)	165.1(2)
O(11)–Ag(1)–O(21c)	82.0(1)	O(22)–Ag(1)–O(21c)	112.9(2)
Ag(1)···Ag(2)–O(12)	88.3(1)	Ag(1)···Ag(2)–O(21)	76.1(1)
Ag(1)···Ag(2)–O(11d)	157.8(1)	O(12)–Ag(2)–O(21)	164.4(2)
O(12)–Ag(2)–O(11d)	113.0(2)	O(21)–Ag(2)–O(11d)	82.6(2)
Ag(1)–O(11)–Ag(2c)	98.4(2)	C(11)–O(11)–Ag(1)	131.0(4)
C(11)–O(11)–Ag(2c)	130.5(3)	C(11)–O(12)–Ag(2)	116.5(4)
Ag(2)–O(21)–Ag(1d)	96.8(2)	C(21)–O(21)–Ag(2)	131.4(4)
C(21)–O(21)–Ag(1d)	129.7(4)	C(21)–O(22)–Ag(1)	115.5(4)
O(11)–C(11)–O(12)	127.1(5)	O(11)–C(11)–C(12)	115.8(5)
O(12)–C(11)–C(12)	117.1(5)	O(21)–C(21)–O(22)	127.4(5)
O(21)–C(21)–C(22)	115.9(5)	O(22)–C(21)–C(22)	116.7(5)

Hydrogen bonding:

O(1W)···O(1)	2.808(7)	O(1W)···O(2W)	2.856(7)
O(2W)···O(2We)	1.777(7)		
O(1)···O(1W)···O(2W)	157.3(5)		
O(1W)···O(2W)···O(2We)	112.6(5)		

$[\{Ag_2(L^1)(NO_3)_2\}_n]$ **3**

Ag(1)···Ag(1b)	2.878(2)	Ag(1)–O(1)	2.273(3)
Ag(1)–O(3)	2.532(5)	Ag(1)–O(1d)	2.567(4)
Ag(1)–O(2b)	2.250(3)	O(1)–C(1)	1.244(5)
O(2)–C(1)	1.251(6)	C(1)–C(2)	1.543(6)
Ag(1b)···Ag(1)–O(1)	76.9(1)	Ag(1b)···Ag(1)–O(1d)	154.5(1)
Ag(1b)···Ag(1)–O(2b)	81.9(1)	Ag(1b)···Ag(1)–O(3)	104.8(1)
O(1)–Ag(1)–O(3)	82.9(1)	O(1)–Ag(1)–O(1d)	79.2(1)
O(3)–Ag(1)–O(1d)	80.8(2)	O(1)–Ag(1)–O(2b)	148.5(1)
O(3)–Ag(1)–O(2b)	125.3(1)	O(1d)–Ag(1)–O(2b)	115.6(1)
Ag(1)–O(1)–Ag(1d)	100.8(1)	C(1)–O(1)–Ag(1)	123.5(3)
C(1)–O(1)–Ag(1d)	131.6(3)	C(1)–O(2)–Ag(1b)	117.2(3)
N(2)–O(3)–Ag(1)	100.4(3)	O(1)–C(1)–O(2)	127.2(4)
O(1)–C(1)–C(2)	114.5(4)	O(2)–C(1)–C(2)	118.2(4)

$[\{Ag_2(L^2)(NO_3)_2\}_n]$ **4**

Ag(1)···Ag(1b)	2.811(1)	Ag(1)–O(1)	2.415(3)
Ag(1)–O(3)	2.496(3)	Ag(1)–O(1d)	2.393(3)
Ag(1)–O(2b)	2.443(3)	Ag(1)–O(4b)	2.424(3)
O(1)–C(1)	1.242(5)	O(2)–C(1)	1.237(4)
C(1)–C(2)	1.554(4)		
Ag(1b)···Ag(1)–O(1)	73.7(1)	Ag(1b)···Ag(1)–O(3)	77.6(1)
Ag(1b)···Ag(1)–O(1d)	158.1(1)	Ag(1b)···Ag(1)–O(2b)	91.0(1)
Ag(1b)···Ag(1)–O(4b)	85.4(1)	O(1)–Ag(1)–O(3)	83.3(1)
O(1)–Ag(1)–O(1d)	85.2(1)	O(3)–Ag(1)–O(1d)	94.4(1)
O(1)–Ag(1)–O(2b)	161.5(1)	O(3)–Ag(1)–O(2b)	83.3(1)
O(1b)–Ag(1)–O(2b)	108.5(1)	O(1)–Ag(1)–O(4b)	104.0(1)
O(3)–Ag(1)–O(4b)	158.9(1)	O(1d)–Ag(1)–O(4b)	105.8(1)
O(2b)–Ag(1)–O(4b)	84.6(1)	Ag(1)–O(1)–Ag(1d)	94.8(1)
C(1)–O(1)–Ag(1)	134.1(2)	C(1)–O(1)–Ag(1d)	131.0(2)
C(1)–O(2)–Ag(1b)	109.6(2)	N(2)–O(3)–Ag(1)	128.1(2)
N(2b)–O(4b)–Ag(1)	123.4(2)	O(1)–C(1)–O(2)	127.4(3)
O(1)–C(1)–C(2)	115.4(3)	O(2)–C(1)–C(2)	117.2(3)

* Symmetry codes: for **1**, (a) $-x, 1-y, 1-z$; (b) $1-x, -y, 1-z$; (c) $1+x, -1+y, z$; (d) $-x, -y, 1-z$; (e) $1+x, y, z$. For **2**, (a) $-x, -y, 2-z$; (b) $2-x, -y, 1-z$; (c) $-1+x, y, z$; (d) $1+x, +y, +z$; (e) $3-x, 1-y, 1-z$. For **3**, (a) $1-x, 1-y, 1-z$; (b) $-x, -y, 1-z$; (c) $-1+x, -1+y, z$; (d) $-x, 1-y, 1-z$; (e) $x, -1+y, z$. For **4**, (a) $1-x, -y, 1-z$; (b) $-x, 1-y, 1-z$; (c) $-1+x, 1+y, z$; (d) $1-x, 1-y, 1-z$; (e) $-1+x, y, z$.

desiccator charged with Drierite for a week to give colourless needle crystals. IR: 3853.8s, 3738.5s, 3676.9m, 3646.2m, 3623.1m, 3023.1w, 2927.1m, 2861.5m, 2361.5s, 2338.5s, 1915.4w, 1869.2vw, 1838.5w, 1746.2m, 1676.9m, 1646.2s, 1623.1s, 1561.5m, 1538.5m, 1500.0s, 1453.8s, 1415.4m, 1392.3s, 1276.9w, 1123.1w, 1053.8w, 961.5m, 823.1m, 800.0w, 669.2w and 576.9vw cm^{-1}.

$[\{Ag_2(L^2)(NO_3)_2\}_n]$ **4**. A mixture of silver(I) nitrate (177.6 mg, 1.0 mmol) and L^2 (82.2 mg, 0.25 mmol) was dissolved in water–ethanol (12 cm^3, 2:1 v/v) with stirring at 60 °C for a few minutes. The resulting solution was allowed to stand in a desiccator charged with Drierite for a few days to yield colourless polyhedral crystals. IR: 3853.8m, 3746.2s, 3676.9m, 3646.2m, 3623.1m, 3123.1m, 3053.8s, 2946.2s, 2861.5m, 2361.5w, 1946.2vw, 1915.4vw, 1869.2w, 1838.5w, 1738.5m, 1646.2w 1516.5s, 1492.2s, 1453.8m, 1423.1w, 1392.3m, 1269.2w, 1215.4w, 1153.8w, 1046.2m, 984.6w, 915.4w, 776.9vw, 746.2w, 676.9w and 630.8w cm^{-1}.

Crystal Structure Determinations.—Information concerning crystallographic data and structure refinement of the four complexes is summarized in Table 1. Intensities were collected in the variable ω-scan mode[23] on a Rigaku AFC7R diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) at 293 K. Unit-cell parameters were calculated from least-squares fitting of 2θ angles for 25 reflections. Crystal stability was monitored by recording three check reflections at intervals of 150 data measurements, and no significant variation was detected. The raw data were processed with a learnt-profile procedure,[24] and empirical absorption corrections based on ψ-scan data were also applied.

All calculations were performed on a PC 486 computer with the SHELXTL-PC program package.[25] Each crystal structure was solved with the Patterson superposition method. The non-hydrogen atoms were refined anisotropically, except for the oxygen atoms of the slightly disordered perchlorate groups in complexes **1** and **2**, which were subjected to interatomic distance constraints of Cl–O 1.42 ± 0.01 Å and O···O 2.31 ± 0.02 Å, and refined isotropically. All the hydrogen atoms were generated geometrically (C–H 0.96 Å), assigned fixed isotropic thermal parameters, and included in the structure-factor calculations. The aqua hydrogen atoms in **2** could not be located. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[26a] The final positional parameters for the four crystal structures, along with their estimated standard

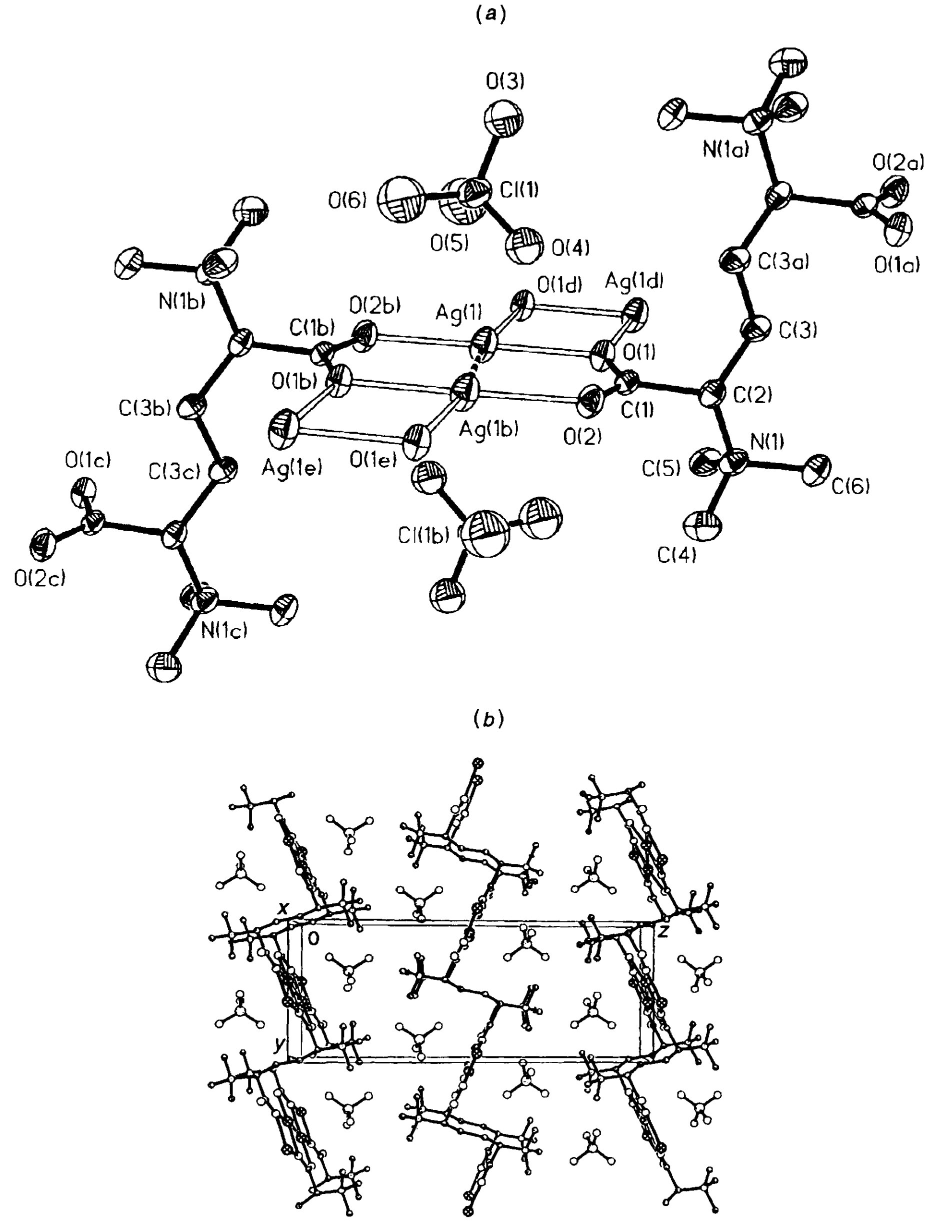


Fig. 2 (*a*) Structural skeleton of the asymmetric unit (35% thermal ellipsoids) of $[\{Ag_2(L^1)\}_n][ClO_4]_{2n}$ **1** with atom labelling and (*b*) packing drawing of the layer structure corresponding to (002) in the crystal structure

deviations, are presented in Table 2 and selected bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprise H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of Structures.—$[\{Ag_2(L^1)\}_n][ClO_4]_{2n}$ **1**. Complex **1** comprises discrete perchlorate anions and a two-dimensional cationic polymeric layer containing bis(carboxylate-*O*,*O*′)-bridged centrosymmetric dimeric subunits [Fig. 2(*a*)]. The Ag···Ag separation [2.810(1) Å] in the dimeric subunit, in which each pair of adjacent silver(I) atoms is doubly bridged by coplanar *syn-syn* μ-carboxylato-*O*,*O*′ groups, is significantly smaller than that (2.89 Å) in metallic silver[26b] and thus suggestive of a stronger metal–metal interaction. The intra-dimer Ag–O distances [2.269(5), 2.249(5) Å] and O–Ag–O angle (164.5°) are comparable to those found in the dimeric structures of known silver(I) betaine complexes.[14,15] The axial positions of the dimer are occupied by oxygen atoms from the carboxylate groups of symmetry-related ligands [Ag–O 2.515(5) Å, Ag···Ag–O 168.9(1)°]. The silver(I) atoms in the present complex is co-ordinated by three carboxylato oxygen atoms in a T-shaped environment [O–Ag–O 82.3(2), 112.5(2)°], and each carboxylate group co-ordinates in the tridentate mode [C(1)–O(1)–Ag(1) 118.0(4), C(1)–O(1)–Ag(1d) 144.1(4), C(1)–O(2)–Ag(1b) 129.8(4)°]. Each pair of adjacent metal atoms are bonded by two kinds of carboxylate bridges, forming a centrosymmetric $[Ag_2(carboxylato\text{-}O,O')_2]$ eight-membered ring and a centrosymmetric rhombic Ag_2O_2 unit. The perchlorate group has no contact with the metal ion < 2.70 Å, and hence such a dimer belong to the typical type D classification. Similar dimer structures have been found for two other betaine complexes, namely $[\{Ag_2(C_5H_5NCH_2CH_2CO_2)_2\}_n][ClO_4]_{2n}$[15] and $[\{Ag_2(Et_3NCH_2CO_2)_2\}_n][ClO_4]_{2n}$,[17] as well as the amino-acid complex glycinesilver(I) nitrate, where the perchlorate or nitrate group is not directly bound to the metal ion. The molecular backbone of the flexible double-betaine ligand is fully extended to achieve maximum separation of its two quaternary nitrogen atoms in the centrosymmetric adipic carbon skeleton [the mean deviation

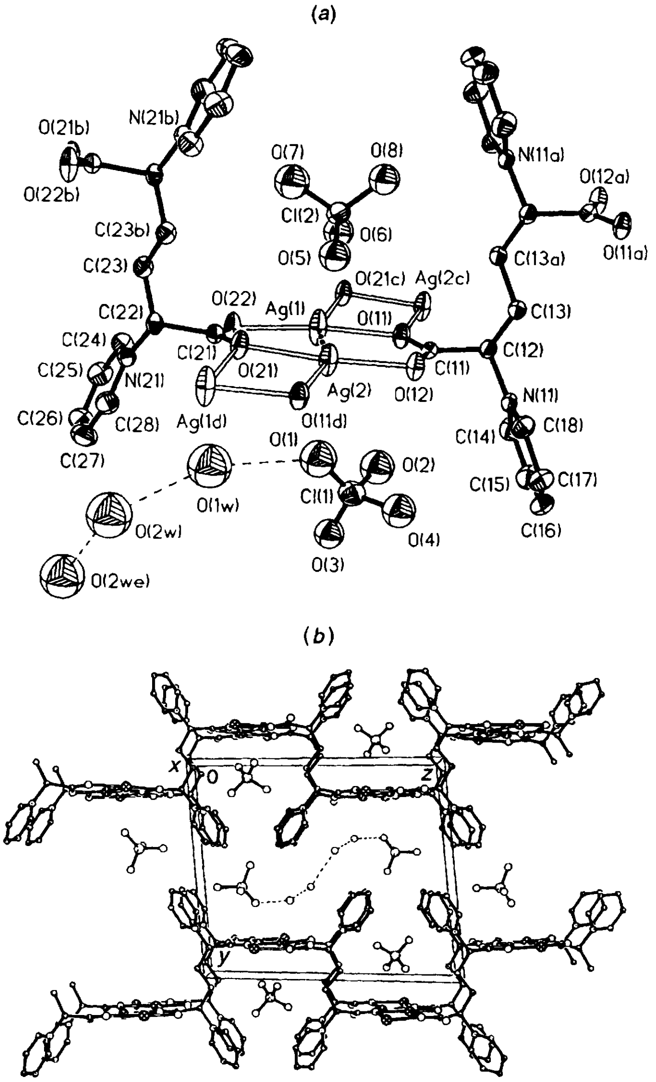


Fig. 3 (*a*) Structural skeleton of the asymmetric unit (35% thermal ellipsoids) of $[\{Ag_2(L^2)\}_n][ClO_4]_{2n}\cdot 2nH_2O$ **2** with atom labelling and (*b*) packing drawing of the layer structure corresponding to (010) in the crystal structure

from the least-squares plane containing atoms N(1), C(2), C(3), C(3a), C(2a) and N(1a) is 0.019 Å], with each carboxylate group deviating from being perpendicular to this plane (dihedral angle 78.6°). The conformation of the double betaine is similar to that in its hydrated form[27] but differs from that in its mercury(II) adducts.[28] A perspective view of complex **1** is shown in Fig. 2(*b*); the dimeric subunits are extended into a step polymeric chain (type D structure) running along the *a* direction. Such chains are cross-linked by the adipic acid skeleton of the double betaine ligand, extending the structure into a sawtooth-wave layer corresponding to the plane (002) with the trimethylammonio groups located at the wave crests. The crystal structure is built up by a packing of these infinite layers such that the interlayer interactions are mainly of the van der Waals type, and the anionic perchlorate groups are packed in the resulting cages.

$[\{Ag_2(L^2)\}_n][ClO_4]_{2n}\cdot 2nH_2O$ **2**. The dimer in complex **2** is similar to that of **1**, being also a type D stairs-like structure based on the bis(carboxylato-*O*,*O*′)bridged dimer [Fig. 3(*a*)]. However, there are two crystallographically independent silver(I) atoms and centrosymmetric double betaine ligands in this complex. The intra-dimer Ag ··· Ag separation [2.794(1) Å], being very close to the shortest one [2.778(5) Å] in an unusual binuclear silver(I) carboxylate, namely bis(3-hydroxy-2,2,3-trimethyl-4-phenylcyclohexanecarboxylato-*O*,*O*′)disilver(I) dihydrate,[12] is considerably shorter (by *ca.* 0.10 Å) than that in metallic silver, thus indicating a significantly stronger metal–metal interaction imposed by the bis(carboxylato-*O*,*O*′) bridges. The intra-dimer Ag–O distances [2.225(4), 2.234(4) for Ag(1); 2.231(4), 2.243(4) Å for Ag(2)] and O–Ag–O angles [165.1(2) for Ag(1), 164.4(2)° for Ag(2)] are comparable to those in complex **1**, whereas the metal–carboxylate linkages [Ag(1)–O(21c) 2.456(5), Ag(2)–O(11d) 2.416(4) Å] between adjacent dimers are significantly shorter than that in complex **1**. The molecular backbone of each double betaine adopts a conformation that is consistant with maximum separation of its pyridinio groups. The carboxylate groups of the two independent double betaine ligands are each nearly perpendicular to the mean plane of the corresponding molecular backbone (dihedral angles 93.5 and 83.5°) comprising the set of atoms N(11), C(12), C(13), C(13a), C(12a) and N(11a) (mean deviation from the plane: 0.046 Å) and the set N(21), C(22), C(23), C(23a), C(22a) and N(21a) (mean deviation from the plane: 0.056 Å), respectively; the dihedral angles made by the pyridine rings are 40.1 and 40.0°. Such a conformation of L^2 is significantly different from that in its hydrate and mercury(II) adducts, in which all the carbon atoms of the molecular skeleton are coplanar with the two pyridine rings nearly perpendicular to the aliphatic skeleton. The most interesting feature in the present complex is that the pair of

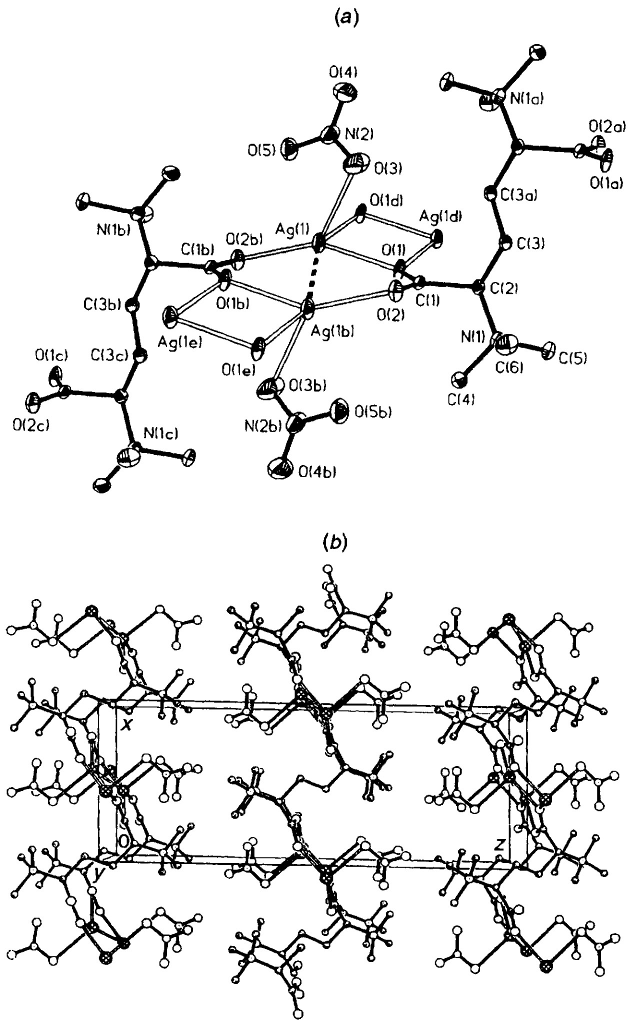


Fig. 4 (*a*) Structural skeleton of the asymmetric unit (35% thermal ellipsoids) of $[\{Ag_2(L^1)(NO_3)_2\}_n]$ **3** with atom labelling and (*b*) packing drawing of the layer structure corresponding to (002) in the crystal structure

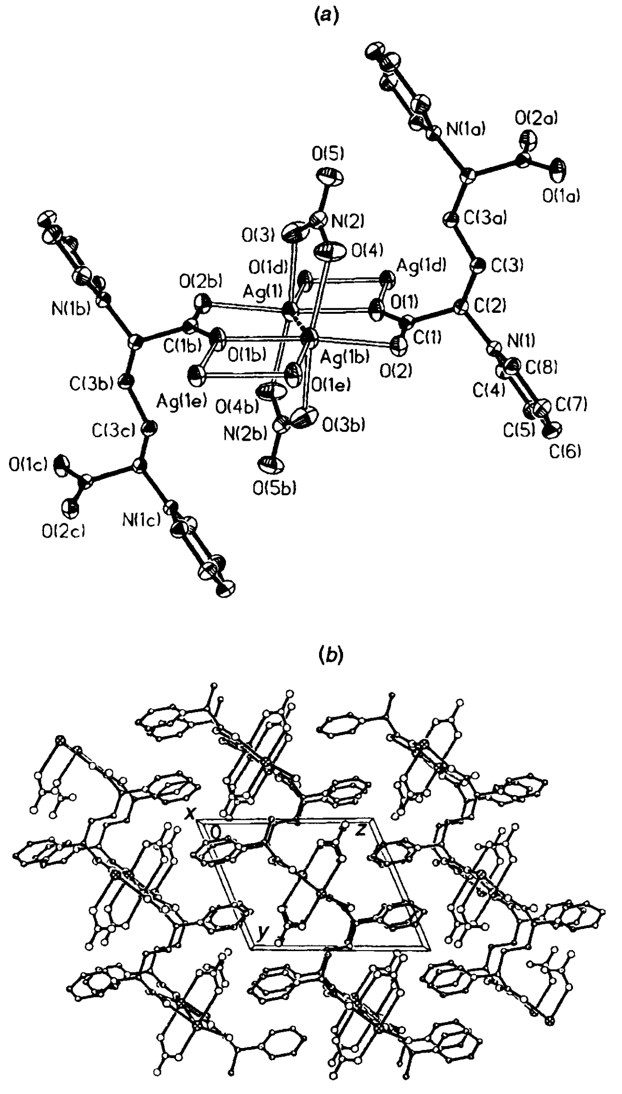


Fig. 5 (*a*) Structural skeleton of the asymmetric unit (35% thermal ellipsoids) of $[\{Ag_2(L^2)(NO_3)_2\}_n]$ **4** with atom labelling and (*b*) packing drawing of the layer structure corresponding to (002) in the crystal structure

crystallographically independent double-betaine ligands bear a *syn* relationship with an approximate C_2 axis passing through the midpoint of the Ag(1) $\cdots$ Ag(2) bond and nearly perpendicular to the [Ag$_2$(carboxylato-*O*,*O*′)$_2$] eight-membered ring [Fig. 3(*a*)]. The crystal structure of complex **2** [Fig. 3(*b*)] reveals an unusual corrugated two-dimensional network corresponding to the (010) plane with pyridine rings located at the turning points and open-side channels pointing in the *a* direction. Both crystallographically independent perchlorate groups exhibit orientational disorder; anions of one type are stacked inside the channels, whereas those of the other type form centrosymmetric hydrogen-bonded 'S-shaped' $(ClO_4^- \cdots H_2O \cdots H_2O \cdots)_2$ units that occupy the inter-layer regions.

$[\{Ag_2(L^1)(NO_3)_2\}_n]$ **3**. Complex **3** has a polymeric structure based on bis(carboxylate-*O*,*O*′)-bridged dimers [Fig. 4(*a*)] with an intra-dimer Ag $\cdots$ Ag distance of 2.878(2) Å, being close to that founded in metallic silver and hence indicative of a comparable metal–metal interaction. The intra-dimer Ag–O distances [2.273(3), 2.250(3) Å] and O–Ag–O angle [148.5(1)°] are comparable to those in **1** and **2**. Unlike the latter complexes, the co-ordination sphere of each silver(I) atom in **3** is completed by a unidentate nitrate ligand [Ag–O 2.532(5) Å] at each axial site of the dimer, apart from metal–carboxylate linkages [Ag–O 2.567(4) Å] between adjacent dimers. The bond angles at the metal centre range from O–Ag–O 79.2(1)° in the centrosymmetric rhombic Ag_2O_2 unit to O–Ag–O 148.5(1)° in the centrosymmetric [Ag$_2$(carboxylato-*O*,*O*′)$_2$] eight-membered ring, so that **3** has a modified type D structure analogous to those of $[\{Ag_2(Me_3NCH_2CH_2CO_2)_2(NO_3)_2\}_n]$,[15] $[\{Ag_2(Me_3NCH_2CO_2)_2(H_2O)_2\}_n][NO_3]_{2n}$ and $[\{Ag_2(C_5H_5NCH_2CO_2)_2(ClO_4)_2\}_n]$.[14] The configuration of the double betaine ligand is close to that in complex **1**, each carboxylate group being nearly perpendicular (95.7°) to the plane of N(1), C(2), C(3), C(3a), C(2a) and N(1a) (mean deviation from the plane: 0.044 Å). The crystal structure of complex **3** is shown in Fig. 4(*b*); the sawtooth-wave two-dimensional polymeric network corresponding to the (002) plane is very similar to that of **1**, except that the nitrate groups are attached to the layers.

$[\{Ag_2(L^2)(NO_3)_2\}_n]$ **4**. Complex **4** is a polymer featuring centrosymmetric bis(carboxylate-*O*,*O*′)-bridged dimers similar to those of type D in **1**–**3**. The intra-dimer Ag $\cdots$ Ag separation [2.811(1) Å] is significantly shorter than that in metallic silver and thus suggestive of a stronger metal–metal interaction. As shown in Fig. 5(*a*), a pair of nitrate anions, oriented nearly perpendicular to the [Ag$_2$(carboxylate-*O*,*O*′)$_2$] plane, link the silver atoms in the *O*,*O*′-bridging mode to generate a paddlewheel-like [Ag$_2$(carboxylate-*O*,*O*′)$_2$(NO$_3$)$_2$] dimer, which is the first example found for silver(I) complexes containing carboxylate-like ligands. The intra-dimer metal–carboxylate linkages [Ag–O 2.415(3), 2.443(3) Å] are significantly longer [by *ca.* 0.15 Å] than those in **1**–**3** and close to the metal–nitrate linkages [2.496(3), 2.424(3) Å], whereas the metal–carboxylate linkages [Ag–O 2.393(3) Å] between adjacent dimers is the shortest among known type D dimers. The silver atom is co-ordinated in an unusual square-pyramidal geometry, the sum of the four basal O–Ag–O angles is 355.2(1)°, and the largest O–Ag–O angle involving the axial oxygen atom is 105.8(1)°. The conformation of the ligand is similar to that in complex **2**; the dihedral angles between the plane containing atoms N(1), C(2), C(3), C(3a), C(2a) and N(1a) with the carboxylate group and pyridine ring are 80.0 and 42.2°, respectively. The crystal structure of complex **4** is shown in Fig. 5(*b*); the wave-like two-dimensional polymeric network corresponding to the (002) plane is very similar to that in **1** and **3**, with the pyridinio rings replacing the trimethylammonio groups.

The present study has demonstrated that two-dimensional co-ordination polymers can be generated from silver(I) perchlorate and silver(I) nitrate with two flexible double betaines. The resulting four complexes in the present study are based on cross-linkage of stair-like type D or modified type D dimers by the double-betaine skeleton. Variation of the quaternary side groups in the adipic acid skeleton of the double betaine, as well as the anions, results in layers of different configurations and co-ordination geometries about the silver(I) atoms.

As expected, the overall charge neutrality of betaine compounds can be used to prepare metal complexes in which the metal centre bears additional anionic ligands. The ligation capability of the anion dictates the co-ordination geometry of silver(I). In complexes **1** and **2**, the perchlorate anions do not interact with the silver(I) atom, which is co-ordinated by three carboxylato oxygen atoms in a T-shaped geometry, and the resulting [Ag$_2$(carboxylate-*O*,*O*′)$_2$] dimer exhibits the typical type D structure. The nitrate anion in complex **3** functions as a unidentate ligand, so that the co-ordination geometry of the silver(I) atom is a distorted tetrahedron, and the [Ag$_2$(carboxylate-*O*,*O*′)$_2$] dimer belongs to a modified type D structure. In contrast to this, the nitrate anion in complex **4** acts in the *O*,*O*′-bridging mode, leading to unusual square-pyramidal five-co-ordination at Ag^I and a novel paddlewheel-like dimeric structural unit, which is the first example of its type among silver(I) carboxylates (Fig. 1).

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