Metal–Betaine Interactions. Part 13.[1] Preparation and Crystal Structures of Four Polymeric Silver(I) Complexes of Betaine Derivatives†

Xiao-Ming Chen and Thomas C. W. Mak *
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Four polymeric silver(I) complexes of the betaine derivatives pyridiniopropionate ($C_5H_5N^+CH_2CH_2CO_2^-$, L^1) and trimethylammoniopropionate ($Me_3N^+CH_2CH_2CO_2^-$, L^2) have been prepared and characterized by X-ray crystallography. The complexes $[(Ag_2L^1{}_2)_n][ClO_4]_{2n}$ **1**, $[\{Ag_2L^1{}_2(NO_3)_2\}_n]$ **2**, $[\{Ag_2L^2{}_2(NO_3)_2\}_n]$ **3** and $[\{Ag_2L^2{}_2(H_2O)\}_n][ClO_4]_{2n}\cdot nH_2O$ **4** all contain bis(carboxylate)-bridged Ag_2 dimer units [Ag–O 2.185(2)–2.264(6), Ag $\cdots$ Ag 2.800(2)–2.901(2) Å] which are extended into stairs-like chains *via* the co-ordination of each metal centre by a carboxylato oxygen atom [Ag–O 2.479(4)–2.588(5) Å] from an adjacent unit. A pair of unidentate nitrate ligands occupy axial co-ordination sites on the same side and on opposite sides of the mean plane of the dimer in **2** and **3**, respectively; the dimer in **4** has only one axial site occupied by an aqua ligand, resulting in uncommon inter-chain metal–metal contacts in the crystal [3.269(2) and 3.346(2) Å].

Most silver(I) carboxylates are composed of either discrete dimers or polymeric chains/networks constructed by the linkage of dimeric subunits, and the structures have been classified previously into four principal types:[2] type A consists of discrete $[Ag_2(\text{carboxylate-}O,O')_2]$ dimers without any axial ligand;[3] B and C have similar dimeric structures with the axial site(s) occupied by one and two ligands, respectively, and they are commonly polymeric species;[2,4] and D comprises dimeric subunits that are extended into a step polymer through the linkage of each metal centre to a carboxylato group of an adjacent dimer,[5,6] while modified type D has an additional axial ligand attached to each metal atom.[7,8] Two unusual polymeric structures that are not based on dimeric units have been classified as a fifth type E.[3,9]

Our recent studies[1] have demonstrated that betaine ($Me_3N^+CH_2CO_2^-$) 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. Furthermore, by virtue of their overall charge neutrality, betaine compounds can be used to prepare metal complexes in which the metal centre can bear additional anionic ligands. Seen in this light, the use of betaines provides a ready synthetic access to new structural varieties of silver(I) carboxylate-like complexes. In previous studies we have determined the crystal structures of several silver(I) complexes of betaines and established some new structural types. For example, both $[\{Ag_2L^3{}_2(H_2O)_2(NO_3)_2\}_n]$ **5** and $[\{Ag_2L^4{}_2(ClO_4)_2\}_n]$ **6** adopt a modified type D structure with additional axial ligands;[7] $[\{AgL^4(NO_3)\}_n]$ **7** is an unusual *catena* complex devoid of dimeric units, which has been classified as a type E complex;[9] and $[Ag_2L^5{}_2(NO_3)_2]$ **8** has uncommon axially bound chelating nitrate ligands[10] (L^3 = trimethylammonioacetate, $Me_3N^+CH_2CO_2^-$; L^4 = pyridinioacetate, $C_5H_5N^+CH_2CO_2^-$; L^5 = triethylammonioacetate, $Et_3N^+CH_2CO_2^-$). This work has now been extended to include the preparation of two new betaine derivatives, pyridiniopropionate ($C_5H_5N^+CH_2CH_2CO_2^-$, L^1) and trimethylammoniopropionate ($Me_3N^+CH_2CH_2CO_2^-$, L^2), and single-crystal X-ray analyses of four polymeric silver(I) complexes, namely bis(pyridiniopropionato)disilver(I) diperchlorate, $[(Ag_2L^1{}_2)_n][ClO_4]_{2n}$ **1**, dinitratobis(pyridiniopropionato)disilver(I), $[\{Ag_2L^1{}_2(NO_3)_2\}_n]$ **2**, dinitratobis(trimethylammoniopropionato)disilver(I), $[\{Ag_2L^2{}_2(NO_3)_2\}_n]$ **3** and aquabis(trimethylammoniopropionato)disilver(I) diperchlorate monohydrate, $[\{Ag_2L^2{}_2(H_2O)\}_n][ClO_4]_{2n}\cdot nH_2O$ **4**.

Experimental

Preparation.—Pyridiniopropionate (L^1). 3-Bromopropionic acid (12.2 g, 0.10 mol) was mixed with pyridine (100 cm^3) and stirred at room temperature overnight. After removal of excess of pyridine under reduced pressure at about 60 °C a yellowish crystalline powder was obtained, which was dissolved in distilled water (15 cm^3), loaded on an Amberlite IRA-93 (OH^- form) anion-exchange column (4.5 × 40 cm), and eluted with distilled water (350 cm^3). The eluate was then evaporated to a yellowish syrup (about 15 cm^3) under reduced pressure using a water-bath at < 70 °C. Trituration with ethanol and acetone afforded a white crystalline product (11.0 g, 91% yield), which is very hygroscopic. ^1H NMR data (CD_3OD, $SiMe_4$ as internal standard): δ 2.85 (2 H, t, CH_2CO), 4.81 (2 H, t, NCH_2), 8.07 (2 H, t, *m*-H of pyridine), 8.55 (1 H, t, *p*-H of pyridine) and 9.02 (2 H, d, *o*-H of pyridine). IR data (KBr): 3292s, 3256s, 3090s, 3063s, 1634s, 1592vs, 1500m, 1489s, 1391s, 984m, 955m, 780m, 729m, 682s and 648m cm^{-1}.

Trimethylammoniopropionate (L^2). This compound was synthesised in a similar manner. A mixture of 3-bromopropionic acid (12.2 g, 0.10 mol) and aqueous trimethylamine (100 cm^3, 40%) was stirred at room temperature overnight. The yellowish powdery residue obtained after evaporation of the resulting solution at *ca.* 70 °C under reduced pressure was dissolved in distilled water (20 cm^3) and passed through an Amberlite IRA-93 (OH^- form) anion-exchange column (4.5 × 42 cm), eluted with distilled water (350 cm^3). The eluate was evaporated to dryness under reduced pressure using a water-bath at < 70 °C to give a white powdery product (9.2 g, 88% yield), which is very hygroscopic. ^1H NMR data (CD_3OD): δ 2.26 (2 H, t, CH_2CO), 3.12 (9 H, s, $3CH_3$) and 3.47 (2 H, t, NCH_2). IR data: 3030s, 3010s, 1602vs, 1483s, 1390s, 1300w, 1251w, 984m, 955m, 927m and 700s (br) cm^{-1}.

$[(Ag_2L^1{}_2)_n][ClO_4]_{2n}$ **1**. To a mixture of $AgClO_4$ (0.207 g, 1.0 mmol) and L^1 (0.151 g, 1.0 mmol) was added distilled water (3

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

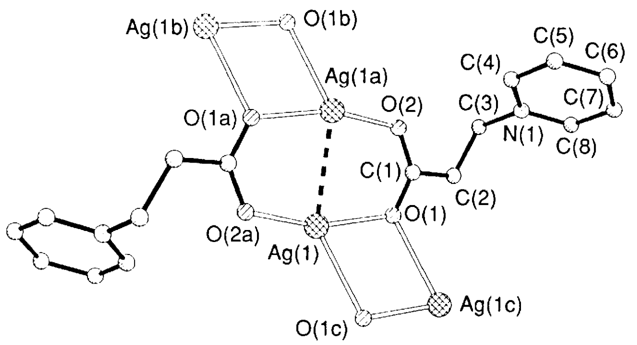

Fig. 1 Perspective view showing the dimeric unit and polymeric structure of the cationic chain in $[(Ag_2L^1{}_2)_n][ClO_4]_{2n}$ **1** and the atom numbering scheme. Symmetry codes as in Table 3

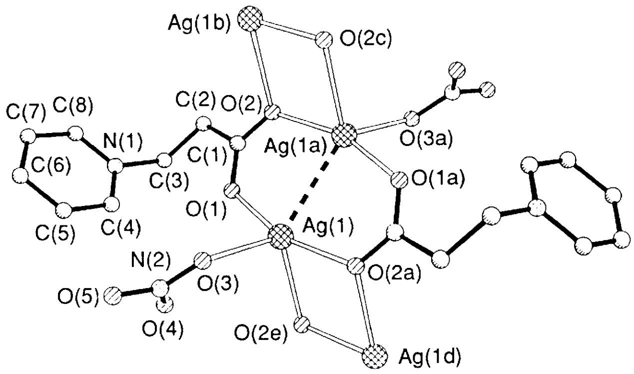

Fig. 2 Perspective view showing the dimeric unit and the polymeric chain in $[\{Ag_2L^1{}_2(NO_3)_2\}_n]$ **2** and the atom numbering scheme. Symmetry codes as in Table 3

cm^3). After stirring at about 60 °C for a few minutes a clear solution was obtained. Standing of the solution in air at room temperature for 10 h yielded colourless prismatic crystals. IR data (KBr): 3135s, 3130s, 3058s, 1620s, 1585vs, 1486s, 1396s, 1143vs, 1118vs, 1078vs, 800m, 689m, 636vs and 624vs cm^{-1}.

$[\{Ag_2L^1{}_2(NO_3)_2\}_n]$ **2**. To a mixture of $AgNO_3$ (0.170 g, 1.0 mmol) and L^1 (0.151 g, 1.0 mmol) was added water–ethanol (4 cm^3, 1:1 v/v). After stirring at 60 °C for 10 min the resulting clear solution was cooled to room temperature. Colourless prismatic crystals were afforded upon evaporation for 2 d in a desiccator charged with silica gel. IR data: 3106vs, 3089vs, 3061vs, 1634s, 1582vs, 1420s, 1385s and 681m cm^{-1}.

$[\{Ag_2L^2{}_2(NO_3)_2\}_n]$ **3**. A mixture of $AgNO_3$ (0.170 g, 1.0 mmol) and L^2 (0.132 g, 1.0 mmol) was added to water–ethanol (4 cm^3, 1:1 v/v) with stirring at 60 °C for 10 min, resulting in a clear solution. After cooling to room temperature, colourless polyhedral crystals were afforded by slow evaporation for several days in a desiccator charged with silica gel. IR data: 3009vs, 3005vs, 1589vs, 1483s, 1391s, 1310s, 940m, 832s and 695m cm^{-1}

$[\{Ag_2L^2{}_2(H_2O)\}_n][ClO_4]_{2n}\cdot nH_2O$ **4**. A mixture of $AgClO_4$ (0.207 g, 1.0 mmol) and L^2 (0.132 g, 1.0 mmol) was dissolved in distilled water (3 cm^3) with stirring at about 60 °C to give a clear solution. After standing in air at room temperature for about 4 h, colourless needle-shaped crystals were obtained. IR data: 3260vs, 3140s, 3050s, 1591vs, 1483s, 1388s, 1145vs, 1130vs, 1082vs, 941m, 640vs and 625m cm^{-1}.

Crystallography.—Densities of the crystals were measured by flotation in 1,2-dibromoethane–CCl_4. Diffraction intensities for the four complexes were collected at 21 °C on a Nicolet R3m/V diffractometer using the ω-scan mode (2.9–14.6° min^{-1}).[11] Data processing, absorption corrections, structure solution, and full-matrix least-squares refinement were performed with the SHELXTL-PLUS program package[12,13] (parameters detailed in Table 1) on a DEC MicroVAX-II computer. The non-hydrogen atoms were refined anisotropically, except for the oxygen atoms of the slightly disordered perchlorate group in complex **4**, which were subjected to interatomic distance constraints of Cl–O 1.41 ± 0.01 Å and O$\cdots$O 2.26 ± 0.01 Å, and refined isotropically. All the hydrogen atoms were generated geometrically (C–H 0.96 Å), assigned isotropic thermal parameters, and included in the structure-factor calculations. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[14a] The final discrepancy indices and other parameters at the conclusion of refinement are listed in Table 1, atomic coordinates in Table 2, and selected interatomic distances and angles in Table 3.

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

Results and Discussion

$[(Ag_2L^1{}_2)_n][ClO_4]_{2n}$ **1**.—Complex **1** is a polymer based on bis(carboxylate-*O,O′*)-bridged centrosymmetrical $Ag_2L^1{}_2$ dimers (Fig. 1), with the carboxylato group of L^1 acting in the *syn–syn* bridging mode [C–O 1.249(4) Å; O–C–O 125.6(3)°]. The Ag$\cdots$Ag separation [2.854(1) Å], mainly constrained by the bis(carboxylate-*O,O′*) bridges, is slightly smaller than that (2.89 Å) in metallic silver[14b] and thus suggestive of a comparable extent of metal–metal interaction. The intra-dimer Ag–O distances and O–Ag–O angle are 2.217(2) and 2.185(2) Å and 161.8(1)°, comparable to those found in the dimeric structures of several known silver(I) carboxylates.[7] The present structure is extended into a stairs-like polymer running parallel to the *b* axis *via* metal–carboxylate linkages [Ag(1)–O(2a) 2.497(2) Å] between adjacent dimers, generating centrosymmetric rhombic Ag_2O_2 units as found in the type D and modified type D structures.[7] The perchlorate group has no association with the metal ion shorter than 2.70 Å, and hence complex **1** belongs to the type D classification. Similar structures have been found for another betaine complex, $[(Ag_2L^5{}_2)_n][ClO_4]_{2n}$, and a complex of an amino acid, glycinesilver(I) nitrate,[4] where the perchlorate or nitrate group is not directly bound to the metal ion. In contrast, a perchlorate group acting as an axial ligand has been found in complex **6** and di-μ-(2-chlorophenoxyethanoato)-disilver(I)–silver(I) perchlorate.[15]

$[\{Ag_2L^1{}_2(NO_3)_2\}_n]$ **2**.—The structure of complex **2** also features bis(carboxylate-*O,O′*)-bridged, centrosymmetrical $Ag_2L^1{}_2$ dimers (Fig. 2) with the L^1 ligand in the symmetrical *syn–syn* bridging mode [C–O 1.258(6) and 1.257(6) Å, O–C–O 126.3(5)°]. The intra-dimer Ag$\cdots$Ag distance [2.901(2) Å], slightly longer than that (2.89 Å) found in metallic silver, indicates a comparable or weaker metal–metal interaction. The intra-dimer Ag–O distances and O–Ag–O angle [Ag–O 2.196(4) and 2.216(6) Å, O–Ag–O 161.0(1)°] are comparable to those in complex **1**. The present dimeric structure is extended into a one-dimensional stairs-like chain running parallel to the *b* axis *via* a metal–carboxylate linkage [Ag(1)–O(2e) 2.552(4) Å] between adjacent dimers, resulting in a rhombic Ag_2O_2 as found in complex **1**. The co-ordination sphere of each metal atom is completed by a unidentate nitrato ligand [2.511(5) Å] at each axial site of the dimer, so that complex **2** is modified type D structure such as those of **6** and bis(μ-benzoato)-bis(pyridine)disilver(I).[8] Although the nitrate group has been found to participate in co-ordination in complex **8** and in alaninesilver(I) nitrate,[6] in the unsymmetrical chelating and bidentate bridging modes, respectively, unidentate nitrate as an axial ligand has not been reported hitherto. Thus complex **2** is a new structural variety among silver(I) carboxylate complexes containing nitrate anions.

$[\{Ag_2L^2{}_2(NO_3)_2\}_n]$ **3**.—Complex **3** is a polymer featuring

Table 1 Data collection and processing parameters[a]

Complex	**1**	**2**	**3**	**4**
Formula	$C_{16}H_{18}Ag_2Cl_2N_2O_{12}$	$C_{16}H_{18}Ag_2N_4O_{10}$	$C_{12}H_{26}Ag_2N_4O_{10}$	$C_{12}H_{30}Ag_2Cl_2N_2O_{14}$
M	716.96	642.12	602.18	713.08
Colour and habit	Colourless prism	Colourless polyhedron	Colourless prism	Colourless needle
$F(000)$	1408	1264	1200	1424
a/Å	29.288(6)	29.43(2)	18.319(6)	5.7000(5)
b/Å	5.5476(8)	5.371(3)	12.440(4)	24.923(8)
c/Å	14.439(2)	13.813(6)	10.479(2)	16.952(4)
β/°	107.47(1)	107.83(1)	119.83(2)	93.25(4)
U/Å^3	2237.8(8)	2079(2)	2071.0(8)	2404.3(9)
D_m/g cm^{-3}	2.120	2.046	1.925	1.980
D_c/g cm^{-3}	2.128	2.052	1.932	1.970
Space group	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$
μ/mm	2.04	1.91	1.93	1.91
Crystal size/mm	0.25 × 0.32 × 0.34	0.16 × 0.22 × 0.30	0.20 × 0.32 × 0.40	0.10 × 0.20 × 0.22
Transmission factors	0.546–0.630	0.466–0.565	0.675–0.891	0.568–0.653
Collection range; $2\theta_{max}$/°	$h, k, \pm l$; 55	$h, k, \pm l$; 55	$h, k, \pm l$; 55	$h, k, \pm l$; 50
Unique data measured	2571	2343	2305	4220
Observed data [$I \geqslant 3\sigma(I)$], n	2019	1558	1795	2696
No. of variables, p	155	146	128	249
$R = \Sigma\Delta/\Sigma\lvert F_o\rvert$[b]	0.026	0.040	0.051	0.050
$R_G = [\Sigma w\Delta^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.029	0.036	0.055	0.063
$S = [\Sigma w\Delta^2/(n-p)]^{\frac{1}{2}}$	1.506	1.722	2.763	1.555
Residual extrema in final difference map (e Å^{-3})	+0.69 to −0.40	+0.67 to −1.25	+1.22 to −0.98	+1.23 to −0.83

[a] Details in common: monoclinic crystal system; $Z = 4$; Mo-Kα radiation (λ 0.710 73 Å); weighting scheme, $w = [\sigma^2(F_o) + K\lvert F_o\rvert^2]^{-1}$, where 10^4K = 1, 1, 1 and 6 for complexes **1**, **2**, **3** and **4**, respectively. [b] $\Delta = \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert$.

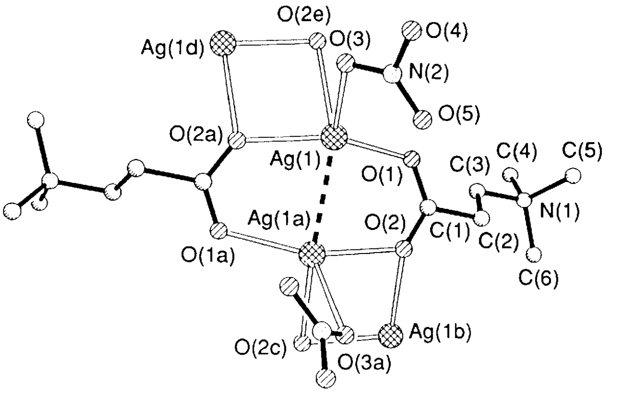

Fig. 3 Perspective view showing the dimeric unit and the polymeric chain in $[\{Ag_2L^2{}_2(NO_3)_2\}_n]$ **3** and the atom numbering scheme. Symmetry codes as in Table 3

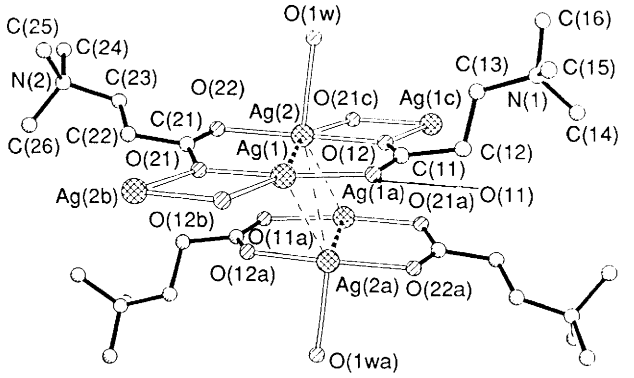

Fig. 4 Perspective view showing the dimeric unit and polymeric structure of the cationic chain in $[\{Ag_2L^2{}_2(H_2O)\}_n][ClO_4]_{2n}{\cdot}nH_2O$ **4** and the atom numbering scheme. Symmetry codes as in Table 3

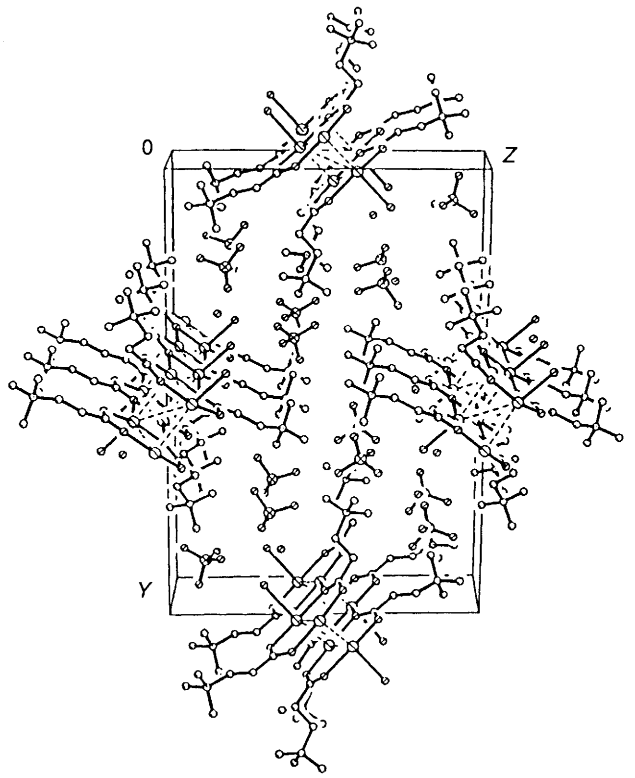

Fig. 5 Molecular packing in complex **4** viewed parallel to the a axis. Metal–metal contacts are represented by thin broken lines

bis(carboxylate-O,O')-bridged $Ag_2L^2{}_2$ dimers of two-fold symmetry (Fig. 3), similar to the centrosymmetrical dimers found in **1** and **2**. The Ag • • • Ag separation [2.800(2) Å], being very close to the shortest one [2.778(5) Å] found in an unusual dinuclear silver(I) carboxylate, namely bis(3-hydroxy-2,2,3-trimethyl-4-phenylcyclohexanecarboxylato)disilver(I) dihydrate,[16] is considerably shorter (by *ca.* 0.09 Å) than that in metallic silver, thus indicating a significantly stronger metal–metal interaction imposed by the bis(carboxylate-O,O') bridges. The carboxylato group exhibits a slightly unsymmetrical *syn–syn* bridging mode [C–O 1.237(8) and 1.254(8) Å, O–C–O 125.6(4)°]. The intra-dimer Ag–O distances and O–Ag–O angle

Table 2 Atomic coordinates (× 10^5 for Ag, × 10^4 for others)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
$[(Ag_2L^1{}_2)_n][ClO_4]_{2n}$ **1**							
Ag(1)	77 575(1)	−4 299(5)	54 671(2)	C(2)	6 978(1)	1 491(6)	2 383(2)
O(3)	8 578(1)	616(6)	5 048(2)	C(3)	6 661(1)	192(7)	1 494(2)
O(4)	9 387(1)	392(8)	5 938(3)	N(1)	6 152(1)	79(5)	1 483(2)
O(5)	8 990(2)	4 121(6)	5 717(3)	C(4)	6 001(1)	−1 722(6)	1 934(2)
O(6)	8 821(1)	1 253(7)	6 712(2)	C(5)	5 528(1)	−1 849(7)	1 917(3)
Cl(1)	8 948(1)	1 613(2)	5 855(1)	C(6)	5 216(1)	−123(8)	1 445(3)
O(1)	7 362(1)	1 208(4)	4 054(2)	C(7)	5 377(1)	1 734(8)	990(3)
O(2)	7 038(1)	−2 135(4)	3 287(2)	C(8)	5 847(1)	1 792(7)	1 016(2)
C(1)	7 130(1)	67(5)	3 317(2)				
$[\{Ag_2L^1{}_2(NO_3)_2\}_n]$ **2**							
Ag(1)	71 891(2)	54 040(8)	45 957(3)	C(2)	6 953(2)	11 362(11)	2 187(4)
O(3)	6 383(2)	4 854(9)	4 834(3)	C(3)	6 617(2)	9 872(11)	1 332(4)
O(4)	6 181(2)	3 116(11)	3 380(4)	N(1)	6 120(2)	9 801(8)	1 386(3)
O(5)	5 656(2)	3 913(13)	4 111(5)	C(4)	5 979(2)	7 935(11)	1 873(5)
N(2)	6 068(2)	3 912(10)	4 098(4)	C(5)	5 523(2)	7 890(13)	1 928(5)
O(1)	6 993(1)	7 829(7)	3 251(3)	C(6)	5 209(2)	9 764(13)	1 471(5)
O(2)	7 399(1)	11 267(7)	3 930(3)	C(7)	5 365(2)	11 677(13)	988(5)
C(1)	7 123(2)	10 047(9)	3 212(4)	C(8)	5 820(2)	11 655(11)	947(4)
$[\{Ag_2L^2{}_2(NO_3)_2\}_n]$ **3**							
Ag(1)	4 475(3)	5 801(4)	17 391(4)	C(1)	1 515(3)	157(4)	4 998(5)
O(3)	644(4)	2 104(4)	382(7)	C(2)	2 310(3)	−106(5)	6 451(6)
O(4)	1 309(3)	3 568(4)	701(6)	C(3)	2 666(3)	−1 182(5)	6 333(6)
O(5)	1 237(6)	2 838(6)	2 454(9)	N(1)	3 453(3)	−1 531(4)	7 725(5)
N(2)	1 038(3)	2 861(4)	1 187(6)	C(4)	3 676(5)	−2 629(5)	7 424(7)
O(1)	1 545(3)	69(4)	3 851(4)	C(5)	4 147(4)	−782(5)	8 032(8)
O(2)	886(2)	453(3)	5 083(4)	C(6)	3 330(5)	−1 598(7)	9 017(7)
$[\{Ag_2L^2{}_2(H_2O)\}_n][ClO_4]_{2n}\cdot nH_2O$ **4**							
Ag(1)	14 713(11)	43 774(3)	1 557(4)	C(23)	1 097(13)	5 569(3)	2 941(4)
Ag(2)	57 356(11)	47 611(3)	9 028(5)	N(2)	−356(11)	5 725(3)	3 631(4)
O(1w)	6 834(33)	4 029(5)	1 940(7)	C(24)	1 340(19)	5 860(5)	4 314(6)
O(11)	3 681(11)	3 879(3)	−569(4)	C(25)	−1 861(18)	5 269(4)	3 870(6)
O(12)	7 040(10)	4 179(3)	1(3)	C(26)	−1 818(19)	6 199(4)	3 420(6)
C(11)	5 851(15)	3 879(3)	−447(5)	Cl(1)	3 955(5)	7 321(1)	3 241(1)
C(12)	7 208(16)	3 461(4)	−906(5)	O(01)	2 149(30)	7 684(6)	3 137(8)
C(13)	8 507(18)	3 110(4)	−323(6)	O(02)	6 105(31)	7 472(8)	3 016(12)
N(1)	9 645(12)	2 615(3)	−682(4)	O(03)	3 433(26)	6 857(5)	2 763(6)
C(14)	11 035(16)	2 746(4)	−1 372(6)	O(04)	4 194(19)	7 135(5)	4 021(5)
C(15)	7 907(19)	2 200(4)	−915(7)	Cl(2)	3 746(5)	4 049(1)	3 919(2)
C(16)	11 267(21)	2 416(5)	−22(7)	O(05)	3 306(22)	4 575(4)	4 121(6)
O(21)	52(10)	4 947(3)	1 015(3)	O(06)	5 906(17)	4 033(5)	3 588(7)
O(22)	3 340(9)	5 164(3)	1 710(3)	O(07)	3 793(20)	3 748(4)	4 606(6)
C(21)	1 193(14)	5 147(3)	1 600(5)	O(08)	1 975(20)	3 879(5)	3 390(7)
C(22)	−332(15)	5 392(4)	2 215(5)	O(2w)	1 542(31)	3 608(5)	1 434(8)

are 2.218(4) and 2.235(3) Å and 153.6(2)°, respectively, comparable to those found in the dimeric structures of several known silver(I) carboxylates. The present structure is extended into a stairs-like polymer running parallel to the *c* axis *via* metal–carboxylate linkages [Ag(1)–O(2e) 2.588(5) Å] between adjacent dimers, generating rhombic Ag_2O_2 units as found in the type D and modified type D structures. It is noteworthy that the pair of axial nitrato ligands [Ag–O(3) 2.499(7) Å], acting in unidentate fashion, lie on the same side of the mean plane of the dimeric unit, giving a new modified type D structure different from those found in bis(μ-benzoato)-bis(pyridine)disilver(I),[8] and complexes **3** and **6**, in which each axial site is occupied by a pyridine, a nitrate and a perchlorate ligand at opposite sides of the Ag_2(carboxylate-*O,O′*)$_2$ dimeric plane, respectively.

$[\{Ag_2L^2{}_2(H_2O)\}_n][ClO_4]_{2n}\cdot nH_2O$ **4**.—Complex **4** is also a stairs-like polymer based on bis(carboxylate-*O,O′*)-bridged dimers (Fig. 4) with an intra-dimer Ag···Ag distance of 2.842(1) Å. The intra-dimer Ag–O distances and O–Ag–O angles range from 2.194(7) to 2.264(6) Å and from 160.1(2) to 166.4(2)°, respectively. The dimeric structure is extended into a one-dimensional stairs-like chain parallel to the *a* axis through metal–carboxylate linkages [Ag–O 2.500(6) and 2.573(6) Å], resulting in rhombic Ag_2O_2 units similar to those found in related complexes. The perchlorate group has no close contact with the metal atom shorter than 2.70 Å. Unlike all the other type D and modified type D structures, only one axial site of the dimer is occupied by an aqua ligand, and thus complex **4** is another new modification of the type D structure. Another uncommon modified type D modification has recently been found in a tetranuclear silver(I) carboxylate, $[\{Ag_2(4\text{-}FC_6H_4CH_2CO_2)_2(H_2O)_2\}_2]$,[17] in which a pair of Ag_2(carboxylate-*O,O′*)$_2$ dimers are linked together through the axial metal–carboxylate weak covalent bonds, generating a centrosymmetrical rhombic Ag_2O_2 unit similar to that found in the type D and other type D modifications, and terminated by an aqua ligand at each axial site of the molecule.

The most interesting feature in complex **4** is that the Ag(1) and Ag(2) atoms in each chain have comparatively short interchain metal–metal contacts with the adjacent cationic

Table 3 Selected interatomic lengths (Å) and bond angles (°)

$[(Ag_2L^1{}_2)_n][ClO_4]_{2n}$ **1**			
Ag(1)–O(1)	2.217(2)	Ag(1)–O(2a)	2.185(2)
Ag(1) · · · Ag(1a)	2.854(1)	O(1)–Ag(1c)	2.497(2)
O(1)–Ag(1) · · · Ag(1a)	80.7(1)	O(1)–Ag(1)–O(1c)	78.0(1)
Ag(1a) · · · Ag(1)–O(1c)	142.0(1)	O(1)–Ag(1)–O(2a)	161.8(1)
Ag(1a) · · · Ag(1)–O(2a)	82.3(1)	O(1c)–Ag(1)–O(2a)	112.2(1)
Ag(1)–O(1)–Ag(1c)	102.0(1)	Ag(1)–O(1)–C(1)	125.2(2)
C(1)–O(1)–Ag(1c)	128.8(2)	C(1)–O(2)–Ag(1a)	125.0(2)
O(1)–C(1)	1.249(4)	O(2)–C(1)	1.249(4)
C(1)–C(2)	1.510(4)	C(3)–N(1)	1.487(5)
O(1)–C(1)–O(2)	125.6(3)	O(1)–C(1)–C(2)	115.8(3)
O(2)–C(1)–C(2)	118.5(3)	C(1)–C(2)–C(3)	116.6(3)
$[\{Ag_2L^1{}_2(NO_3)_2\}_n]$ **2**			
Ag(1)–O(1)	2.196(4)	Ag(1)–O(2a)	2.216(4)
Ag(1)–O(3)	2.511(5)	Ag(1)–O(2e)	2.552(4)
Ag(1) · · · Ag(1a)	2.901(2)		
O(3)–Ag(1)–O(1)	99.6(2)	O(3)–Ag(1) · · · Ag(1a)	123.5(1)
O(1)–Ag(1) · · · Ag(1a)	80.6(1)	O(3)–Ag(1)–O(2e)	106.7(2)
O(1)–Ag(1)–O(2e)	104.0(1)	Ag(1a) · · · Ag(1)–O(2e)	128.4(1)
O(3)–Ag(1)–O(2a)	96.0(2)	O(1)–Ag(1)–O(2a)	161.0(1)
Ag(1a) · · · Ag(1)–O(2a)	81.8(1)	O(2e)–Ag(1)–O(2a)	81.6(2)
Ag(1)–O(3)–N(2)	115.8(4)	Ag(1b)–O(2)–Ag(1a)	98.4(2)
Ag(1)–O(1)–C(1)	126.4(3)	C(1)–O(2)–Ag(1b)	124.6(3)
C(1)–O(2)–Ag(1a)	123.6(3)		
O(3)–N(2)	1.253(6)	O(4)–N(2)	1.216(9)
O(5)–N(2)	1.219(9)	O(1)–C(1)	1.257(6)
O(2)–C(1)	1.258(6)	C(1)–C(2)	1.523(8)
O(3)–N(2)–O(4)	119.0(6)	O(3)–N(2)–O(5)	118.7(6)
O(4)–N(2)–O(5)	122.3(6)	O(1)–C(1)–O(2)	126.3(5)
O(1)–C(1)–C(2)	117.5(4)	O(2)–C(1)–C(2)	116.1(5)
$[\{Ag_2L^2{}_2(NO_3)_2\}_n]$ **3**			
Ag(1)–O(1)	2.218(4)	Ag(1)–O(2a)	2.235(3)
Ag(1)–O(3)	2.499(7)	Ag(1)–O(2e)	2.588(5)
Ag(1) · · · Ag(1a)	2.800(2)		
O(3)–Ag(1)–O(1)	118.0(2)	O(3)–Ag(1) · · · Ag(1a)	128.0(2)
O(1)–Ag(1) · · · Ag(1a)	85.9(1)	O(3)–Ag(1)–O(2a)	88.4(2)
O(1)–Ag(1)–O(2a)	153.6(2)	Ag(1a) · · · Ag(1)–O(2a)	77.6(1)
O(3)–Ag(1)–O(2e)	79.2(2)	O(1)–Ag(1)–O(2e)	95.6(2)
Ag(1a) · · · Ag(1)–O(2e)	148.0(1)	O(2a)–Ag(1)–O(2e)	87.9(2)
Ag(1a)–O(2)–Ag(1b)	92.1(2)	Ag(1)–O(3)–N(2)	113.0(5)
Ag(1)–O(1)–C(1)	119.2(4)	C(1)–O(2)–Ag(1a)	127.8(3)
C(1)–O(2)–Ag(1b)	120.3(3)		
O(3)–N(2)	1.229(7)	O(4)–N(2)	1.237(9)
O(5)–N(2)	1.19(1)	O(1)–C(1)	1.237(8)
O(2)–C(1)	1.254(8)	C(1)–C(2)	1.530(6)
O(3)–N(2)–O(4)	118.7(7)	O(3)–N(2)–O(5)	119.8(8)
O(4)–N(2)–O(5)	120.9(6)	O(1)–C(1)–O(2)	125.6(4)
O(1)–C(1)–C(2)	117.9(6)	O(2)–C(1)–C(2)	116.5(5)
C(1)–C(2)–C(3)	110.0(4)		
$[\{Ag_2L^2{}_2(H_2O)\}_n][ClO_4]_{2n}\cdot nH_2O$ **4**			
Ag(1)–O(11)	2.194(7)	Ag(1)–O(21)	2.218(6)
Ag(2)–O(12)	2.264(6)	Ag(2)–O(22)	2.226(6)
Ag(1)–O(12b)	2.573(6)	Ag(2)–O(1w)	2.59(1)
Ag(2)–O(21c)	2.500(6)	Ag(1) · · · Ag(2)	2.842(1)
Ag(1) · · · Ag(2a)	3.269(2)	Ag(2) · · · Ag(2a)	3.346(2)
Ag(2) · · · Ag(1)–O(11)	86.4(2)	Ag(2) · · · Ag(1)–O(21)	80.0(1)
O(11)–Ag(1)–O(21)	166.4(2)	Ag(2) · · · Ag(1)–O(12b)	157.0(1)
O(11)–Ag(1)–O(12b)	115.2(2)	O(21)–Ag(1)–O(12b)	78.3(2)
Ag(2a) · · · Ag(1)–O(12b)	125.2(1)	Ag(1) · · · Ag(2)–O(1w)	103.5(4)
Ag(1) · · · Ag(2)–O(12)	77.8(1)	O(1w)–Ag(2)–O(12)	86.0(3)
Ag(1) · · · Ag(2)–O(22)	83.5(1)	O(1w)–Ag(2)–O(22)	91.9(4)
O(12)–Ag(2)–O(22)	160.1(2)	Ag(1) · · · Ag(2)–O(21c)	155.4(1)
O(1w)–Ag(2)–O(21c)	83.1(4)		
O(22)–Ag(2)–O(21c)	120.4(2)	O(12)–Ag(2)–O(21c)	79.1(2)
Ag(2)–O(12)–C(11)	127.7(5)	Ag(1)–O(11)–C(11)	120.3(6)
C(11)–O(12)–Ag(1c)	132.7(6)	Ag(2)–O(12)–Ag(1c)	99.5(2)
Ag(1)–O(21)–Ag(2b)	103.1(2)	Ag(1)–O(21)–C(21)	125.5(5)
Ag(2)–O(22)–C(21)	122.1(5)	C(21)–O(21)–Ag(2b)	126.6(5)
O(11)–C(11)	1.24(1)	O(12)–C(11)	1.24(1)
C(11)–C(12)	1.54(1)	O(21)–C(21)	1.26(1)
O(22)–C(21)	1.228(9)	C(21)–C(22)	1.52(1)
O(11)–C(11)–O(12)	127.4(8)	O(11)–C(11)–C(12)	116.1(8)
O(12)–C(11)–C(12)	116.5(7)	C(11)–C(12)–C(13)	108.0(7)
O(21)–C(21)–O(22)	126.8(8)	O(21)–C(21)–C(22)	114.2(7)
O(22)–C(21)–C(22)	119.0(7)	C(21)–C(22)–C(23)	112.0(7)

Symmetry codes: for **1**, a $\frac{3}{2}-x, -\frac{1}{2}-y, 1-z$; b $x, -1+y, z$; c $\frac{3}{2}-x, \frac{1}{2}-y, 1-z$; for **2**, a $\frac{3}{2}-x, \frac{3}{2}-y, 1-z$; b $x, 1+y, z$; c $\frac{3}{2}-x, \frac{5}{2}-y, 1-z$; d $\frac{3}{2}-x, \frac{1}{2}-y, 1-z$; e $x, -1+y, z$; for **3**, a $-x, y, \frac{1}{2}-z$; b $x, -y, \frac{1}{2}+z$; c $-x, -y, -z$; for **4**, a $1-x, 1-y, -z$; b $-1+x, y, z$; c $1+x, y, z$.

polymeric chain in the 'co-facial' fashion as illustrated in Fig. 5. Although these interatomic distances [Ag(1) · · · Ag(2a) 3.269(2), Ag(2) · · · Ag(2a) 2.346(2) Å] are significantly longer than the corresponding contacts found in the dimeric silver(I) carboxylates, and in metallic silver as well, they are significantly shorter than twice the van der Waals radius of silver (2 × 1.72 = 3.44 Å),[18] and may play a significant role in the mode of crystal packing.

Acknowledgements

This work was supported by a Hong Kong UPGC Earmarked Grant for Research (Acc. no. 221300010).

References

1 Part 12, X.-M. Chen and T. C. W. Mak, *Struct. Chem.*, 1991, in the press.

2 T. C. W. Mak, W. H. Yip, C. H. L. Kennard, G. Smith and E. J. O'Reilly, *Aust. J. Chem.*, 1986, **39**, 541.

3 G. Smith, C. H. L. Kennard and T. C. W. Mak, *Z. Kristallogr.*, 1988, **184**, 275; B. T. Usubaliev, E. M. Movsumov, I. R. Amiraslanov, A. I. Akhmedov, A. A. Musaev and Kh. S. Mameov, *Zh. Strukt. Khim.*, 1981, **22**, 98.

4 J. K. M. Rao and M. A. Viswamitra, *Acta Crystallogr., Sect. B*, 1972, **28**, 1484.

5 R. G. Griffin, J. D. Ellett, M. Mehring, J. G. Bullitt and J. S. Waugh, *J. Chem. Phys.*, 1972, **57**, 2147.

6 M. E. Kamwaya, E. Papavinasam, S. G. Teoh and R. K. Rajaram, *Acta Crystallogr., Sect. C*, 1984, **40**, 1318.

7 X.-M. Chen and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1991, 1219.

8 M. Hedrich and H. Hartl, *Acta Crystallogr., Sect. C*, 1983, **39**, 533.

9 X.-M. Chen and T. C. W. Mak, *Polyhedron*, 1991, in the press.

10 W.-Y. Huang, L. Lü, X.-M. Chen and T. C. W. Mak, *Polyhedron*, 1991, in the press.

11 R. A. Sparks, in *Crystallographic Computing Techniques*, ed. F. R. Ahmed, Munksgaard, Copenhagen, 1977, p. 452.

12 G. M. Sheldrick, in *Computational Crystallography*, ed. D. Sayre, Oxford University Press, New York, 1982, p. 506.

13 G. M. Sheldrick, in *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, New York, 1985, p. 175.

14 *International Tables for X-Ray Crystallography*, Kynoch Press,

Birmingham, 1974, (*a*) vol. 4, pp. 55, 99 and 149; (*b*) vol. 3, p. 278 (now distributed by Kluwer Academic Publishers, Dordrecht).

15 T. C. W. Mak, W. H. Yip, C. H. L. Kennard, G. Smith and E. J. O'Reilly, *J. Chem. Soc., Dalton Trans.*, 1988, 2353.

16 P. Coggon and A. T. McPhail, *J. Chem. Soc., Chem. Commun.*, 1972, 91.

17 G. Smith, D. S. Sagatys, C. A. Campbell, D. E. Lynch and C. Kennard, *Aust. J. Chem.*, 1990, **43**, 1707.

18 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

Received 4*th June* 1991; *Paper* 1/02672K