Preparation and Crystal Structures of the Silver(I) Carboxylates $[Ag_2\{C_6H_4(CO_2)_2\}(NH_3)_2]$, $[NH_4][Ag_5\{C_6H_3(CO_2)_3\}_2(NH_3)_2(H_2O)_2]\cdot H_2O$ and $[NH_4][Ag\{C_4H_2N_2(CO_2)_2\}]$†

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Two silver ammine complexes with the polyprotic aromatic acids benzene-1,2-diacarboxylic acid (phthalic acid) and benzene-1,3,5-tricarboxylic acid (trimesic acid) have been prepared and their structures determined using single-crystal X-ray diffraction and infrared spectroscopy. Complex **1**, $[Ag_2\{C_6H_4(CO_2)_2\}(NH_3)_2]$, is a hydrogen-bonded polymer based on a simple diamminephthalatodisilver(I) species, with an ammonia molecule and a single phthalate carboxylate oxygen bonded to separate silver atoms, giving essentially linear co-ordination [Ag–N 2.116(3), Ag–O 2.134(2) Å, O–Ag–N 175.3(1)°]. All three ammine hydrogens are involved in intermolecular hydrogen-bonding interactions, giving a chain polymer. Complex **2**, $[NH_4][Ag_5\{C_6H_3(CO_2)_3\}_2(NH_3)_2(H_2O)_2]\cdot H_2O$, is a two-dimensional sheet polymer based on a pseudo-centrosymmetric *S*-type trimer unit, linked by the carboxylate groups of two independent trimesate residues [Ag···Ag 2.928(1), 2.946(1) Å]. The two ammonia molecules are also bonded linearly to two independent silvers [Ag–N 2.141(6), 2.159(7) Å; N–Ag–O 166.1(2), 170.2(2)°]. The terminal silvers provide bonding links to adjacent trimesate carboxyl oxygens between the layers while the third trimesate carboxyl group forms conventional centrosymmetric bis[(carboxylato-*O,O'*)silver(I)] dimers [Ag···Ag 2.847(1), 2.856(4) Å], with water molecules in the axial sites for the dimer. A third compound **3**, ammonium silver(I) pyrazine-2,3-dicarboxylate $[NH_4][Ag\{C_4H_2N_2(CO_2)_2\}]$, has also been prepared using a procedure similar to that for **1** and **2**. However, unlike them, it has no bonded ammines but has a distorted trigonal-planar co-ordination involving two carboxylate oxygens [Ag–O 2.333(6), 2.376(5) Å] and one heteronitrogen [Ag–N 2.249(6) Å], from three separate ligand molecules, giving a polymer structure.

The diamminesilver(I) ion represents a classical archetypal silver structure, with the textbook linear stereochemistry arising from sp hybridization about silver. The early crystal structure determination of $[Ag(NH_3)_2]_2SO_4$ by Corey and Wyckoff[2] confirmed the presence of discrete cations and anions in the solid state; this linear cationic species was also being found in the structures of $[Ag(NH_3)_2]NO_3$[3] {and the isomorphous $[Ag(NH_3)_2]ClO_4$[4]}, $[Ag(NH_3)_2]BF_4$,[5] $[Ag(NH_3)_2][Ag(NO_2)_2]$[6] and in a number of other silver ammine complexes. With the determination of the crystal structures of an increasing number of silver complexes, particularly of those with carboxylic acids, of which surprisingly few examples were known[7] until work by our group, tetrahedral and trigonal stereochemistries now appear more 'normal' than linear for silver(I). Our interest in the structural chemistry of silver(I) carboxylates has resulted in the determination of more than thirty structures and allowed classification of the structure types,[8] the majority being based on bis(carboxylato-*O,O'*) dimers. These dimers may be discrete, such as in silver(I) benzoate[9] or salicylate,[10] or they may be extended in the axial sites of the dimer into tetramers [*e.g.* silver(I) (4-fluorophenoxy)acetate hydrate[11]] or polymers [silver(I) phenoxyacetate[11]]. Less common is the presence of an oxygen-donor group of a smaller molecule such as a water [silver(I) *N*-acetylanthranilate hydrate[12]] or a perchlorate [silver(I) (2-chlorophenoxy)acetate–silver(I) perchlorate[13]] in these sites. Open structures are also found, having essentially linear two-co-ordinate silvers [*e.g.* silver(I) (4-chloro-2-methylphenoxy)acetate[13] (zigzag chain polymer), silver(I) fumarate[1] (figure-of-eight ring polymer) and silver(I) nicotinate[12] (helical chain polymer). In these the co-ordination about silver is either linear or trigonal planar.

The preparation of silver carboxylates under aqueous conditions often results in the formation of very insoluble 'silver salts', for which crystal-structure determination is difficult, requiring special conditions for crystal growth, *e.g.* gel permeation (silver succinate[14]). With other cases in which the silver salt is moderately water soluble, *e.g.* silver(I) hydrogen (+)-tartrate monohydrate,[15] solubility is enhanced by the hydrophilic nature of the acid and the product is atypical, with a structure more closely related to those of the Group 1 metal (+)-tartrates and hydrogen (+)-tartrates (distorted-octahedral six-co-ordinate, with no carboxylato-*O,O'* links). The use of ammoniacal conditions to enhance the solubility of the silver carboxylates has been the preferred method employed by our group for preparing crystalline products for X-ray analysis.[8] Under these conditions most silver(I) complexes involving monocarboxylic acids result in the incorporation of no ammonium ion, exceptions being ammonium silver(I) nicotinate monohydrate[12] and ammonium silver(I) *N*-acetylanthranilate dihydrate.[12] However, polycarboxylic acids, because of the

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† Silver(I) Carboxylates. Part 13.

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steric constraints imposed on the crystallizing system by the multiple functional groups, show a greater tendency, even in the presence of an excess of silver ions, to incorporate an ammonium counter ion, *e.g.* ammonium silver(I) citrate (3-carboxy-3-hydroxypentane-1,5-dioate) monohydrate.[16] These constraints are more acute when an aromatic acid such as phthalic acid (benzene-1,2-dicarboxylic acid) or trimesic acid (benzene-1,3,5-tricarboxylic acid) is used. The preparation of the silver salts of both of these acids under ammoniacal conditions gave products with an elemental analysis (C, H, N) indicative of an unusual stoichiometry, consistent with the presence of ammine substitution in the complexes $[Ag_2\{C_6H_4(CO_2)_2\}(NH_3)_2]$ **1** and $[NH_4][Ag_5\{C_6H_3(CO_2)_3\}_2(NH_3)_2(H_2O)_2]\cdot H_2O$ **2**. The infrared spectrum for **2** was not conclusive enough to confirm the presence of co-ordinated ammine (because of interfering frequencies due to the ammonium ion, water and carboxylates in the critical interpretative regions). However, that of **1** and both the crystal structure determinations and chemical analyses for **1** and **2** enabled the confirmation of the presence of co-ordinated ammine in both, representing the first structural evidence for this phenomenon in silver(I) carboxylates. Also reported is the crystal structure of the silver complex with a dicarboxylic acid analogous to phthalic acid, ammonium silver(I) pyrazine-2,3-dicarboxylate $[NH_4][Ag\{C_4H_2N_2(CO_2)_2\}]$ **3**, in which no ammine incorporation is found.

Experimental

Preparation.—Compound **2** was prepared using a previously described procedure[8] by interacting 1:3 stoichiometric amounts of benzene-1,3,5-tricarboxylic acid (trimesic acid) (0.21 g, 1 mmol) and silver nitrate (0.51 g, 3 mmol) in a total volume of *ca.* 30 cm^3 of 10% aqueous ammonia solution. Compound **1** was prepared using a similar procedure except that potassium hydrogenphthalate (0.20 g, 1 mmol) was used instead of phthalic acid, with $AgNO_3$ (0.34 g, 2 mmol), in a total volume of *ca.* 30 cm^3 of 10% ammonia solution. Allowing the solutions partially to evaporate at room temperature in the dark over several weeks gave large colourless needle prisms of **1** (0.30 g, 75% yield) and flattened prisms of **2** (0.45 g, 42% yield) (Found: C, 23.1; H, 2.4; N, 6.6. Calc. for $C_8H_{10}Ag_2N_2O_4$ **1**: C, 23.2; H, 2.4; N, 6.8. Found: C, 20.2; H, 2.1; N, 3.9. Calc. for $C_{18}H_{22}Ag_5N_3O_{15}$ **2**: C, 20.7; H, 2.1; N, 4.0%). Compound **3** was prepared in a similar manner to that of **1** by using 1:2 stoichiometric amounts of pyrazine-2,3-dicarboxylic acid (0.14 g, 1 mmol) and silver nitrate (0.34 g, 2 mmol) in a total volume of 20 cm^3 of 10% aqueous ammonia solution. Yellow crystals began to form from the colourless solution after standing for 3 d (0.25 g, 86% yield). These crystals were hard, chemically stable and relatively photoinsensitive (Found: C, 23.9; H, 2.0; N, 14.1. Calc. for $C_6H_6AgN_3O_4$: C, 24.7; H, 2.0; N, 14.4%). All specimens used for X-ray analysis were cleaved from larger crystals. Infrared spectra were completed on all samples as rapidly pressed discs in KBr, using a Perkin-Elmer 1600 series FTIR spectrometer.

Crystallography.—Crystal data. $C_8H_{10}Ag_2N_2O_4$ **1**, M_r = 413.9, monoclinic, space group $C2/c$, a = 12.108(1), b = 8.143(1), c = 11.942(1) Å, β = 115.394(5)°, U = 1063.7(2) Å^3, Z = 4, D_c = 2.585, D_m = 2.60 g cm^{-3}, $F(000)$ = 792, λ = 0.710 73 Å, μ(Mo-Kα) = 36.8 cm^{-1}, T = 298(2) K.

$C_{18}H_{22}Ag_5N_3O_{15}$ **2**, M_r = 1059.7, monoclinic, space group $P2_1/n$, a = 7.236(3), b = 16.897(3), c = 20.52(1) Å, β = 99.62(2)°, U = 2474(2) Å^3, Z = 4, D_c = 2.846, D_m = 2.83 g cm^{-3}, $F(000)$ = 2024, λ = 0.710 73 Å, μ(Mo-Kα) = 39.7 cm^{-1}, T = 298(2) K.

$C_6H_6AgN_3O_4$ **3**, M_r = 292.0, triclinic, space group $P\bar{1}$, a = 6.838(4), b = 7.885(2), c = 8.072(7) Å, α = 84.54(4), β = 69.65(6), γ = 80.34(4)°, U = 402.2(4) Å^3, Z = 2, D_c = 2.411, D_m = 2.40 g cm^{-3}, $F(000)$ = 284, λ = 0.710 73 Å, μ(Mo-Kα) = 25.0 cm^{-1}, T = 298(2) K.

Data collection, structure solution and refinement. X-Ray diffraction data were collected from crystals measuring 0.25 × 0.18 × 0.15 (**1**), 0.25 × 0.20 × 0.12 (**2**) and 0.42 × 0.20 × 0.18 mm (**3**) on an Enraf-Nonius CAD-4 diffractometer, using graphite-crystal monochromatized Mo-Kα radiation. Of 939 (**1**), 4716 (**2**) and 1411 (**3**) unique reflections collected up to $2\theta_{max}$ = 50°, 877 (**1**), 4349 (**2**) and 1221 (**3**) with $F_o > 4.0\sigma(F_o)$ were considered observed and used in the expression of the unweighted refinement residuals; $R1$ $[= \Sigma(||F_o| - |F_c||/|F_o|)]$, $wR2$ $\{= [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{\frac{1}{2}}\}$, with $w = [\sigma^2 F_o^2 + (AP)^2 + BP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Collection ranges were: for **1**, h 0–14, k 0–9, l −14 to 12; for **2**, h 0–8, k 0–19, l −24 to 24; for **3**, h 0–8, k −9 to 9, l −8 to 9. The data were corrected for absorption using empirical methods (MOLEN[17]). The structures were solved using the Patterson procedure of SHELXS 86[18] and refined by full-matrix least squares (SHELXL 93[19]) to residuals $R1$, $wR2$ and S of 0.025, 0.089, 0.61 (**1**), 0.092, 0.33, 1.10 (**2**) and 0.055, 0.138, 1.07 (**3**) respectively. For **1**, A = 0.150, B = 2.55; for **2**, A = 0.0293, B = 4.9 and for **3**, A = 0.106, B = 0.0. Number of parameters: 94 (**1**), 458 (**2**) and 152 (**3**). Remaining electron-density peaks: 0.476, −0.648 (**1**); 0.549, −0.607 (**2**); and 1.524, −2.095 e Å^{-3} (**3**). For all compounds hydrogen atoms were located by difference methods and included in the respective refinements with both positional and isotropic thermal parameters refined. Atomic coordinates for compounds **1**–**3** are given in Table 1, selected bond distances and angles in Table 2.

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

Discussion

$[Ag_2\{C_6H_4(CO_2)_2\}(NH_3)_2]$ **1**.—In the structure of diamminesilver(I) phthalate the 'outer' oxygen of each phthalate carboxyl group is bonded to a silver ion [Ag(1)–O(12) 2.134(2) Å] (Fig. 1). These complex units have molecular symmetry coincident with crystallographically imposed two-fold rotational symmetry. In the sites *trans* to these oxygens are found the ammine groups [Ag(1)–N(1) 2.116(3) Å, N(1)–Ag(1)–O(12) 175.3(1)°]. This Ag–N value compares with 2.110(3) Å in diamminesilver(I) perchlorate[5] and 2.15(3) Å in diamminesilver(I) tetrahydroborate.[5] The Ag–O(carboxyl) distance compares with typical values of 2.18–2.20 Å in the bis(carboxylato-*O,O′*) dimer[10] and 2.19–2.22 Å in the open carboxyl-bridged polymer structures.[13] An unusual feature of the present structure is the presence of parallel associations between the

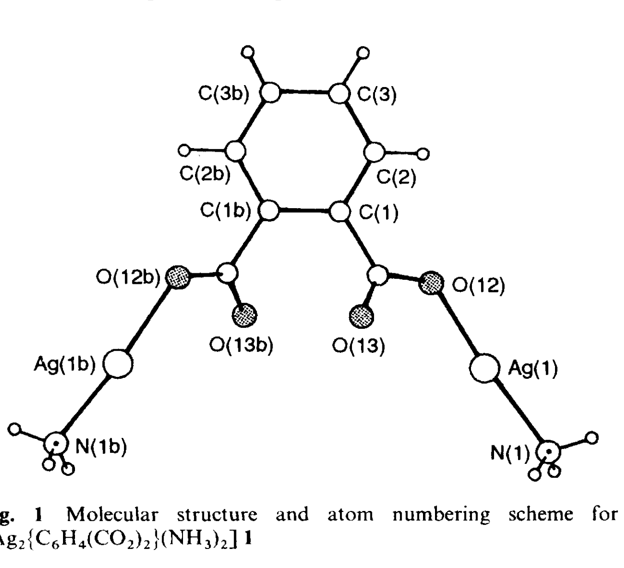

Fig. 1 Molecular structure and atom numbering scheme for $[Ag_2\{C_6H_4(CO_2)_2\}(NH_3)_2]$ **1**

linear O–Ag–N bonds across inversion centres in the cell. These have silver–silver separations [Ag(1)···Ag(1a)] of 3.244(1) Å (a $\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$), with hydrogen bonding between all three ammine hydrogens, and the carboxyl oxygens [N(1)–H(31)···O(12a) 3.089(4) Å, N–H···O 160°; N(1)–H(13)···O(13c) 3.108(4) Å, N–H···O 157° (c $\frac{1}{2} + x$, $\frac{1}{2} + y$, z); N(1)–H(11)···O(13d) 2.994(4) Å, N–H···O 174° (d $1 - x$, $1 - y$, $1 - z$)]. This results in a two-dimensional hydrogen-bonded sheet structure which extends across the *bc* direction of the cell (Fig. 2). The hydrogen bonds also form links between the sheets *via* the unco-ordinated carboxyl oxygens. The phthalate residues are similar to that found in the structure of the parent acid,[20] with the carboxylate groups lying considerably out of the plane of the benzene ring [torsion angle O(12)–C(11)–C(1)–C(2) −47.4(2)°, *cf.* −32.7° in the parent].

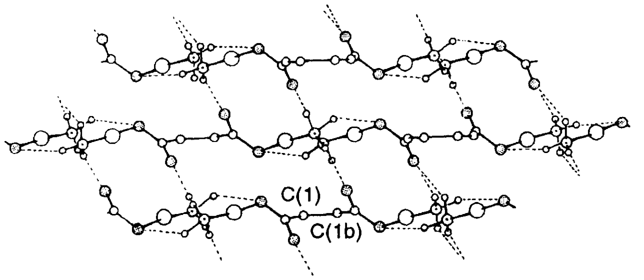

Fig. 2 Packing of complex **1** in the unit cell showing hydrogen-bonding associations. The view is down the phthalate rings with all ring carbons except C(1) and C(1b) omitted for clarity

$[NH_4][Ag_5\{C_6H_3(CO_2)_3\}_2(NH_3)_2(H_2O)_2]\cdot H_2O$ **2**.—The polymeric layer structure has at its centre a unique open S-type structural unit (Fig. 3), comprising three silver atoms [Ag(1), Ag(3) and Ag(2)] linked by carboxylato-*O,O'* bridges from the two trimesate residues [Ag(1)–O(322) 2.183(4), Ag(3)–O(332f) 2.107(4), Ag(2)–O(321) 2.165(4), Ag(3)–O(331a) 2.105(5) Å]. This gives Ag(1)···Ag(3) and Ag(2)···Ag(3) separations of 2.928(1) and 2.946(1) Å respectively, while the O–Ag–O bond angle at the pseudo-inversion centre [Ag(3)] is 178.5(2)°. In the sites *trans* to the outer carboxyl oxygens are the two ammine groups, giving a bonding mode similar to that of complex **1**. The Ag(1)–N(3) and Ag(2)–N(2) distances are 2.141(6) and 2.159(7)

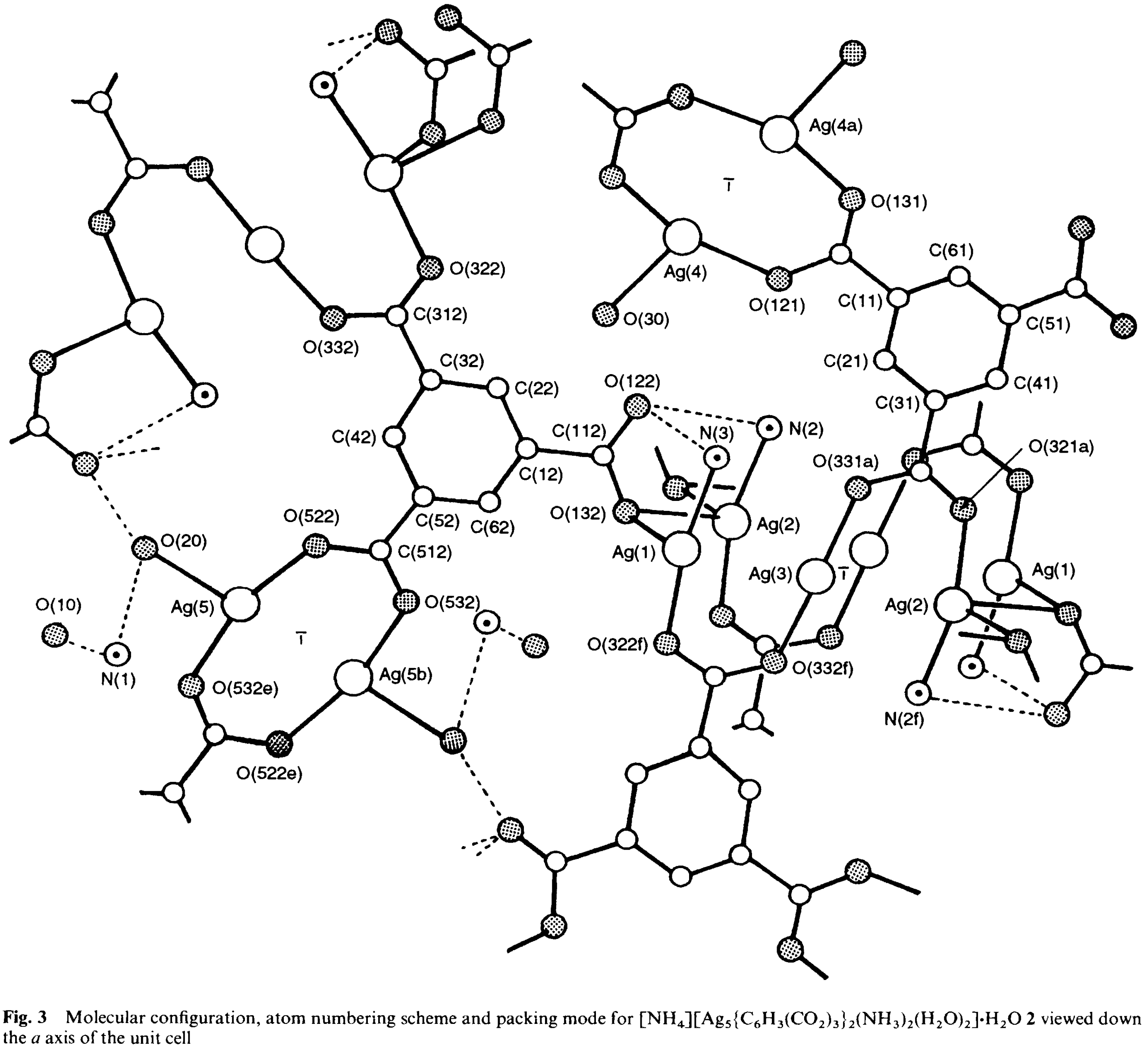

Fig. 3 Molecular configuration, atom numbering scheme and packing mode for $[NH_4][Ag_5\{C_6H_3(CO_2)_3\}_2(NH_3)_2(H_2O)_2]\cdot H_2O$ **2** viewed down the *a* axis of the unit cell

Table 1 Atomic coordinates (× 10⁴) for $[Ag\{C_6H_4(CO_2)_2\}(NH_3)_2]$ **1**, $[NH_4][Ag_5\{C_6H_3(CO_2)_3\}_2(NH_3)_2(H_2O)_2]\cdot H_2O$ **2** and $[NH_4][Ag\{C_4H_2N_2(CO_2)_2\}]$ **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **1**							
Ag(1)	3117(1)	3359(1)	4181(1)	C(3)	4679(3)	−3477(4)	2860(3)
N(1)	2776(3)	5419(3)	5067(3)	C(11)	4412(2)	1058(4)	3367(2)
C(1)	4678(2)	−512(3)	2870(2)	O(12)	3344(2)	1179(3)	3310(3)
C(2)	4366(3)	−2003(4)	3219(3)	O(13)	5225(2)	2091(3)	3839(2)
Complex **2**							
Ag(1)	910(3)	5576(1)	1143(1)	C(22)	3402(26)	7784(10)	2978(8)
Ag(2)	3956(3)	4328(1)	−1127(1)	C(32)	3039(25)	7987(11)	3613(8)
Ag(3)	2562(3)	4961(1)	37(1)	C(42)	2576(25)	7389(11)	4009(9)
Ag(4)	288(3)	9462(1)	542(1)	C(52)	2417(27)	6599(10)	3791(8)
Ag(5)	242(3)	5568(1)	5524(1)	C(62)	2792(22)	6420(11)	3183(9)
C(11)	−2595(25)	6694(10)	3834(9)	C(112)	3671(24)	6790(11)	2085(9)
C(21)	−2446(26)	7461(10)	4066(9)	C(312)	1808(26)	3826(10)	1133(8)
C(31)	−1974(23)	8067(10)	3674(8)	C(512)	1764(27)	5982(10)	4228(8)
C(41)	−1584(25)	7909(10)	3045(8)	O(122)	3668(23)	7322(8)	1660(7)
C(51)	−1686(25)	7131(11)	2811(9)	O(132)	3862(21)	6054(8)	1964(7)
C(61)	−2216(25)	6530(10)	3229(9)	O(322)	1292(23)	4358(7)	1508(7)
C(111)	−3202(26)	6063(11)	4272(9)	O(332)	2185(24)	3917(8)	568(7)
C(311)	3165(29)	6100(11)	−1061(9)	O(522)	1331(20)	5337(7)	3993(6)
C(511)	−1252(24)	6914(10)	2138(8)	O(532)	1726(22)	6191(9)	4828(7)
O(121)	−3612(20)	5387(8)	4022(6)	N(1)	−259(28)	4758(10)	2644(9)
O(131)	−3313(22)	6259(9)	4856(6)	N(2)	4277(27)	3214(11)	−591(8)
O(321)	3504(27)	5546(8)	−1435(8)	N(3)	571(28)	6694(11)	635(9)
O(331)	2911(23)	6019(8)	−466(7)	O(10)	−4422(26)	4752(10)	2770(8)
O(521)	−1105(21)	6189(7)	2015(6)	O(20)	1085(24)	6445(9)	6486(7)
O(531)	−1124(21)	7464(8)	1730(6)	O(30)	3337(24)	3826(10)	3433(8)
C(12)	3315(24)	7006(10)	2764(9)				
Complex **3**							
Ag(1)	1332(1)	7917(1)	6732(1)	C(21)	2077(10)	6129(9)	−228(9)
N(1)	2864(9)	3877(7)	1779(8)	O(21)	2451(9)	5016(7)	−1351(7)
C(2)	2282(10)	5569(9)	1560(9)	O(22)	1573(9)	7735(6)	−445(7)
C(3)	1901(10)	6715(8)	2888(9)	C(31)	1077(11)	8631(9)	2798(9)
N(4)	2203(8)	6178(7)	4424(7)	O(31)	2394(8)	9655(6)	2390(8)
C(5)	2821(11)	4516(9)	4611(10)	O(32)	−886(8)	9028(6)	3315(7)
C(6)	3117(11)	3352(9)	3309(10)	N(10)	3163(10)	1395(9)	8957(9)

Table 2 Selected bond distances (Å) and angles (°) for complexes **1**–**3**

Complex **1**				Complex **1**			
Ag(1)–O(12)	2.134(2)	Ag(1)–N(1)	2.116(3)	O(12)–Ag(1)–N(1)	175.3(1)		
Complex **2**				Complex **2**			
Ag(1)–O(322)	2.183(4)	Ag(4)–O(131a)	2.215(4)	O(322)–Ag(1)–N(3)	170.2(2)	O(521)–Ag(2)–O(132)	87.3(6)
Ag(1)–N(3)	2.141(6)	Ag(4)–O(30)	2.435(6)	O(322)–Ag(1)–O(132)	91.7(2)	O(331)–Ag(3)–O(332)	178.5(2)
Ag(1)–O(132)	2.601(4)	Ag(5)–O(532)	2.190(4)	N(3)–Ag(1)–O(132)	93.9(3)	O(121)–Ag(4)–O(131)	163.4(2)
Ag(2)–O(321)	2.165(4)	Ag(5)–O(522b)	2.222(4)	O(321)–Ag(2)–N(2)	166.1(2)	O(121)–Ag(4)–O(30)	97.7(2)
Ag(2)–N(2)	2.159(7)	Ag(5)–O(20)	2.436(6)	O(321)–Ag(2)–O(521)	92.9(2)	O(131)–Ag(4)–O(30)	98.7(2)
Ag(2)–O(521)	2.660(4)	Ag(1) ··· Ag(3)	2.928(1)	O(321)–Ag(2)–O(132)	97.8(2)	O(532)–Ag(5)–O(522b)	164.4(2)
Ag(2)–O(132)	2.591(4)	Ag(2) ··· Ag(3)	2.946(1)	N(2)–Ag(2)–O(521)	93.9(2)	O(532)–Ag(5)–O(20)	99.0(2)
Ag(3)–O(331)	2.105(5)	Ag(4) ··· Ag(4a)	2.847(1)	N(2)–Ag(2)–O(132)	93.9(3)	O(522b)–Ag(5)–O(20)	96.6(2)
Ag(3)–O(332)	2.107(4)	Ag(5) ··· Ag(5b)	2.856(4)				
Ag(4)–O(121)	2.253(4)						
Complex **3**				Complex **3**			
Ag(1)–N(4)	2.249(6)	Ag(1)–O(32b)	2.376(5)	N(4)–Ag(1)–O(22a)	137.4(2)	O(22a)–Ag(1)–O(32b)	92.3(2)
Ag(1)–O(22a)	2.333(6)			N(4)–Ag(1)–O(32b)	127.6(2)		

Symmetry relations: for complex **2**, a $-x, 1-y, 1-z$; b $-x, 1-y, -z$; for **3**, a $x, y, 1+z$; b $-x, 2-y, 1-z$.

Å [*cf.* 2.116(3) Å in **1**], with close to linear O–Ag–N angles [170.2(2) and 166.1(2)° respectively]. The outer pseudo-inversion-related silvers [Ag(1) and Ag(2)] are also bonded to a single oxygen [O(132)] of the carboxyl group of the second trimesate residue giving layers down the short (*a*) crystallographic axis [Ag(1)–O(132) 2.610(4), Ag(2)–O(132) 2.591(4) Å, Ag–O–Ag 90.9(2)°]. The Ag(1) ··· Ag(2) separation (1 + *x*, *y*, *z*) is 3.517(2) Å. Hydrogen bonding stabilizes the structure, *via* interactions between the ammine group and the unco-ordinated carboxyl oxygen of the second trimesate [O(122) ··· N(3) 3.00, O(122) ··· N(2) 2.99 Å]. The third carboxylate group of each trimesate is involved in co-ordination to the fourth and fifth

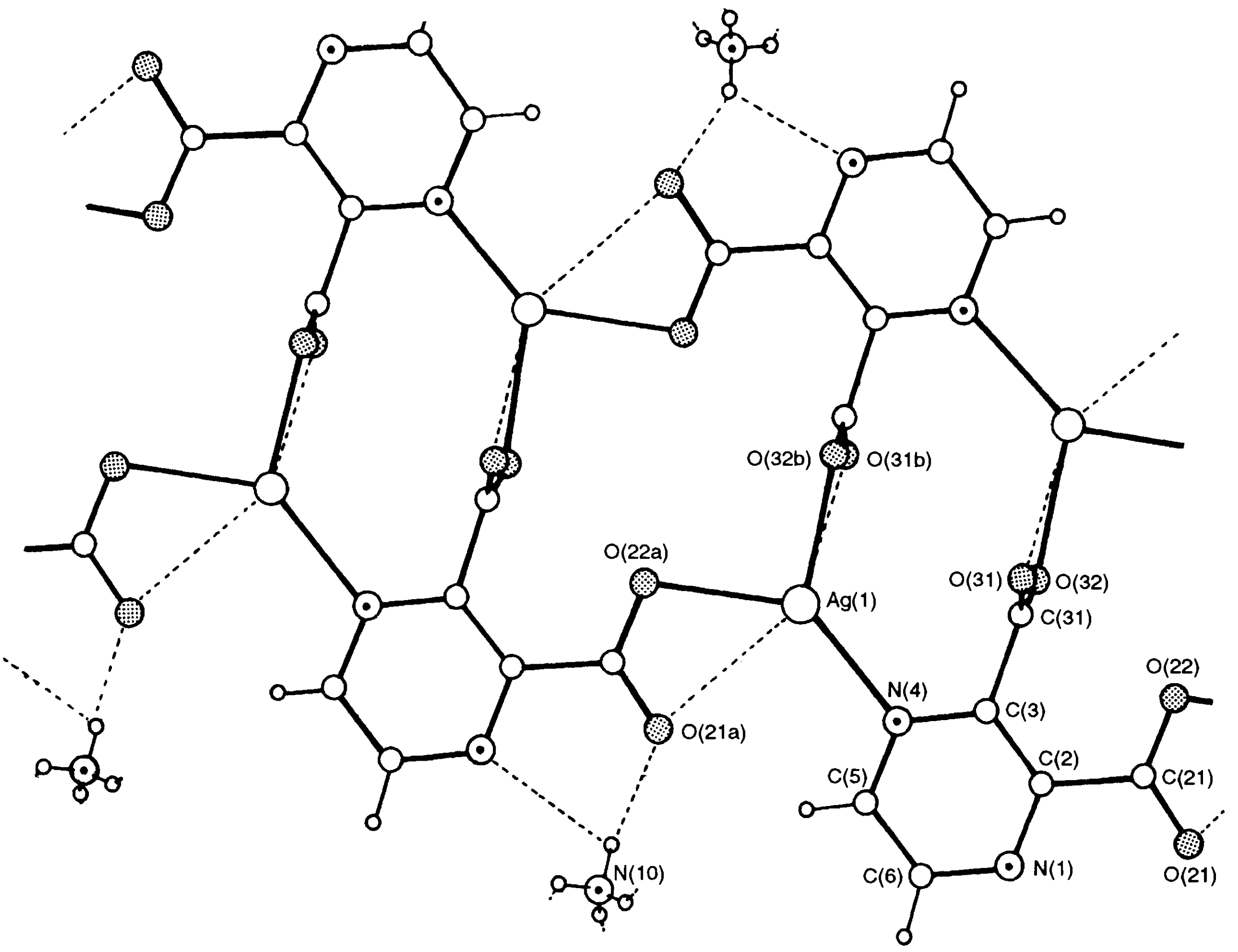

Fig. 4 Molecular structure and atom numbering scheme for $[NH_4][Ag\{C_4H_2N_2(CO_2)_2\}]$ **3**

silvers [Ag(4)–O(121) 2.253(4), Ag(4)–O(131d) 2.215(4) (d $-x$, $2-y$, $-z$); Ag(5)–O(522e) 2.222(4), Ag(5)–O(532) 2.190(4) Å (e $1-x$, $-y$, $-z$) *via* two centrosymmetric bis(carboxylato-*O,O'*) dimers. These dimers have inversion symmetry, similar to a large number of silver(I) carboxylates[8] [Ag(4)···Ag(4a) 2.847(1) (a $-x$, $1-y$, $1-z$); Ag(5)···Ag(5b) 2.856(1) Å (b $-x$, $1-y$, $-z$)]. In the terminal sites of these dimers are found water molecules, such as is in silver *N*-acetylanthranilate dihydrate[12] [Ag(4)–O(30) 2.435(6), Ag(5)–O(20) 2.436(6) Å], giving Type 2 dimers.[8] These waters are also hydrogen bonded to the free carboxylate groups [O(20)···O(122) 2.78 Å] and to the ammonium ion [O(20)···N(1) 2.83 Å]. The ammonium ion and the lattice water [O(10)] are involved in a number of additional hydrogen-bonding interactions with carboxylate oxygens.

$[NH_4][Ag\{C_4H_2N_2(CO_2)_2\}]$ **3**.—The structure of ammonium silver(I) pyrazine-2,3-dicarboxylate **3** forms a ribbon polymer based on distorted trigonal-planar three-co-ordinate silver centres. These involve one bond to a pyrazine nitrogen [Ag(1)–N(4) 2.249(6) Å] and two bonds to symmetry-related carboxylate oxygens [Ag(1)–O(22a) 2.333(6) Å (a x, y, $1+z$); Ag(1)–O(32b) 2.376(5) Å (b $-x$, $2-y$, $1-z$) (Fig. 4). The second carboxyl oxygens of each group also give weaker asymmetric bidentate associations with silver [Ag–O(21a) 2.821(6), Ag–O(31b) 2.825(6) Å]. This co-ordination mode is similar to that found in ammonium silver(I) nicotinate monohydrate[12] except that the trigonal centres in **3** are of the AgO_2N type rather than $AgON_2$. Furthermore the presence of the two carboxylate groups results in open centrosymmetric 14-membered rings which accommodate the ammonium ions through association. The pyrazine rings comprising the 'ends' are offset by half the cell parameter down the *a*-cell direction, which probably contributes to the yellow colour observed for this compound. A number of hydrogen-bonding associations are found between the ammonium ion [N(10)] and both pyrazine nitrogens and carboxylate oxygens, within and between the ribbons [within N(10)···N(1) 3.05, N(10)···O(21) 2.82; between N(10)···O(31) 2.91, N(10)···O(31) 2.85, N(10)···O(22) 3.20, N(10)···O(32) 2.86 Å].

The carboxylate groups adopt different conformations, one being almost coplanar with the pyrazine ring, the other almost perpendicular [torsion angles N(1)–C(2)–C(21)–O(21) 0.03, N(4)–C(3)–C(31)–O(31) 82.5° respectively]. This contrasts with the parent acid where both are equal and inclined (145.4°).[21]

Infrared Spectroscopy.—The use of infrared spectroscopy to identify the presence of co-ordinated ammine molecules in silver carboxylate complexes presents difficulties, not only with respect to sample preparation (as pressed KBr discs) but also in the occurrence of the fundamental vibrational frequencies in the regions of the spectrum where both carboxylate and aromatic ring vibrations are found. This problem is made insoluble where ammonium ions and both co-ordinated and lattice waters are present, as in the case of the trimesate complex **2**. Identification in this case is based on the crystal structure and on elemental analysis. However, with the anhydrous silver ammine phthalate structure **1** (in the absence of both NH_4^+ and H_2O), the broad absorption band (3425 cm^{-1}) can be due only to ammonia which, together with the presence of a weak ν(Ag–N) absorption at 424 cm^{-1} is consistent with silver–ammine co-ordination. This latter value compares with the 400 cm^{-1} found for symmetrical silver(I) ammines, *e.g.* $[Ag(NH_3)_2]_2SO_4$,[22] and represents a shift to higher frequency consistent with the presence of three hydrogen-bonding associations involving the ammonia. The NH_3 deformation frequency is also recognized as a partially resolved peak at *ca.* 1610 cm^{-1} while the aromatic frequencies do not allow identification of the $\rho_r(NH_3)$ frequency in the region 600–750 cm^{-1}. The magnitude of the splitting parameter Δ for the carboxyl ν(C–O) frequencies (1560 and 1384 cm^{-1} respectively) is 176 cm^{-1} which is similar to the values found for both ionic acetate (164 cm^{-1})[23] and bridging acetate [as distinct from the smaller values for chelating (bidentate) acetate[24]]. With the trimesate complex **2**, in which both bridging and unidentate carboxylates are found, the value of Δ cannot be determined with any certainty.

With complexes **1** and **2** the phenomenon of formation of mixed carboxylate–ammine co-ordination complexes with silver(I) under similar preparative conditions, whilst it has no precedent in the chemical literature, it is not unexpected. The steric constraints imposed by the aromatic ring systems on the carboxylic acid groups in both **1** and **2** make it difficult to involve all of these in conventional bis(carboxylato-*O,O'*) silver(I) dimer associations. Therefore, the ammonia molecules act in a space-filling capacity, occupying the sites *trans* to the carboxyl oxygen. No known examples exist where a water molecule occupies the *trans* site to the carboxylate oxygen in silver carboxylates, the water invariably occupying the axial dimer sites. In such examples, this bond is considerably elongated [*e.g.* 2.52 Å,[12] *cf.* 2.13 Å for the Ag–O (carboxyl) bond in complex **1**].

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