Silver(I)–Phenoxyalkanoates. The Crystal and Molecular Structures of Polymeric [(4-Chloro-2-methylphenoxy)ethanoato-*O,O′*]silver(I), [(2,4-Dichlorophenoxy)ethanoato-*O,O′*]silver(I), and Di-μ-[(2-chlorophenoxy)ethanoato-*O,O′*]-disilver(I)–Silver(I) Perchlorate (1/1)†

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The crystal structures of three polymeric silver(I) phenoxyalkanoates have been determined by *X*-ray diffraction. The isomorphous complexes, [(4-chloro-2-methylphenoxy)ethanoato]silver(I) (**1**) and [(2,4-dichlorophenoxy)ethanoato]silver(I) (**2**) are chain polymers of the type $[\{AgL\}_n]$ and involve only two-co-ordinate linear bonds to silver [Ag–O, 2.185(3)—2.217(3) Å; O–Ag–O, 176.8(2), 177.5(2)°]. Complex (**1**) is monoclinic, space group $P2_1/n$, $Z = 8$, in a cell with $a = 9.100(2)$, $b = 13.503(6)$, $c = 15.702(5)$ Å, $\beta = 100.12(2)°$, and was refined to $R = 0.053$ for 2 743 observed reflections. Complex (**2**) was confirmed as isomorphous and isostructural with (**1**) using single-crystal and *X*-ray powder diffractometry. Di-μ-[(2-chlorophenoxy)ethanoato]-disilver(I)–silver(I) perchlorate, $[\{Ag_2L_2{\cdot}AgClO_4\}_n]$, (**3**), forms triclinic crystals, space group $P\bar{1}$, with $Z = 2$, in a cell of dimensions $a = 10.245(2)$, $b = 10.798(2)$, $c = 11.067(2)$ Å, $\alpha = 75.27(2)$, $\beta = 68.27(2)$, $\gamma = 82.70(2)°$. The structure was refined to $R = 0.052$ for 3 661 observed reflections. Complex (**3**) is a sheet polymer based on bis(carboxylate) bridged Ag_2L_2 units [Ag–O, 2.229(4)—2.299(4) Å]. In the two axial sites of the dimers are a co-ordinated perchlorate group [Ag–O, 2.454(4) Å] and a bridging carboxyl oxygen [Ag–O, 2.373(4) Å], while an angular bridge is also formed between the centrosymmetrically related dimer pairs by the third silver [Ag–O, 2.322(4), 2.296(4) Å; O–Ag–O, 126.4(4)°].

Structural studies of the divalent metal complexes of the phenoxyalkanoic acids have been extended to include those with silver(I). Two examples of this series are known, $[Ag_2L_2]$ [L = (2,3,4,5,6-pentafluorophenoxy)ethanoate][1] and $[\{Ag_2L'_2\}_n]$ [L′ = (2-carbamoylphenoxy)ethanoate].[2] All known silver(I) carboxylates form bis(carboxylate-*O,O′*) bridged dimers or dimer polymers which have been classified[2] into four categories depending on the co-ordination motif. 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, terminal oxygens extend the structure into a polymer through adjacent carboxyl groups. The pentafluoro- and carbamoyl-substituted phenoxyalkanoate complexes are of types A and B respectively. The series of complexes reported here involve the herbicidally active acids (4-chloro-2-methylphenoxy)ethanoic acid (cmpe), (2,4-dichlorophenoxy)ethanoic acid (dcpe), and (2-chlorophenoxy)ethanoic acid (cpe). The complexes obtained with cmpe [(**1**)] and dcpe [(**2**)] were found to be isomorphous, with an empirical formula [AgL]. With (2-chlorophenoxy)ethanoic acid, the product obtained using $AgClO_4$ was found to be less susceptible to photodecomposition than that obtained from $AgNO_3$. Furthermore, cell data and a density measurement indicated that $AgClO_4$ was incorporated in crystals of this compound giving an empirical formula $[Ag_2L_2{\cdot}AgClO_4]$, (**3**) [L = (2-chlorophenoxy)ethanoate]. This was subsequently shown to be a type D dimer polymer but with axially co-ordinated perchlorates as well as an angular, two-co-ordinate silver bridge.

Experimental

Preparation of the Complexes.—The complexes $[\{Ag(O_2CCH_2OC_6H_3Me\text{-}2,Cl\text{-}4)\}_n]$, (**1**), and $[\{Ag(O_2CCH_2OC_6H_3Cl_2\text{-}2,4)\}_n]$, (**2**), were prepared by adding hot solutions (ethanol–water, 40:10 cm^3) containing 0.01 mol of (4-chloro-2-methylphenoxy)ethanoic acid, for (**1**), or (2,4-dichlorophenoxy)ethanoic acid, for (**2**), to aqueous ammoniacal silver nitrate (40 cm^3 of a 0.01 mol dm^{-3} solution). The latter was prepared by dissolving $AgNO_3$ in a minimum volume of water and adding 15 mol dm^{-3} ammonia solution dropwise to dissolve the AgOH precipitate. Ammonia was also added to the reaction mixture to remove any precipitate. This was heated on a steam-bath for *ca.* 2 h. After standing in the dark for several weeks, large colourless block prisms of the silver complexes were formed.

Complex (**3**) was prepared from (2-chlorophenoxy)ethanoic acid in a similar manner with silver perchorate replacing silver nitrate.

Infrared spectra, elemental analysis, and single-crystal *X*-ray diffraction photographs for (**2**) indicated that (**1**) and (**2**) were isomorphous. Powder samples of (**1**) and (**2**) were also analysed using *X*-ray powder diffractometry. The diffraction pattern obtained for (**1**) was indexed using the single-crystal data. The pattern for (**2**) was then indexed and the cell dimensions were determined by least-squares refinement using the 2θ angles for 18 reflections up to 2θ = 35° (Co-K_α radiation, λ = 1.788 9 Å).

Crystal Data, Structure Solution, and Refinement.—Details of unit cells for compounds (**1**), (**2**), and (**3**) and data collection and refinement for compounds (**1**) and (**3**) are listed in Table

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† *Supplementary data available* (No. SUP 56708, 4 pp.): *X*-ray powder diffraction data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Details of cell data and structure refinement for [{Ag($O_2CCH_2OC_6H_3$Me-2,Cl-4)}$_n$], (**1**), and [{$Ag_2(O_2CCH_2OC_6H_4$Cl-2$)_2$·$AgClO_4$}$_n$], (**3**)

	(**1**)[a]	(**3**)
Formula	$C_9H_8AgClO_3$	$C_{16}H_{12}Ag_3Cl_3O_{10}$
Symmetry	Monoclinic	Triclinic
M	307.5	794.2
a/Å	9.100(2)	10.245(2)
b/Å	13.503(6)	10.798(2)
c/Å	15.702(5)	11.067(2)
α/°	90	75.27(2)
β/°	100.12(2)	68.27(2)
γ/°	90	82.70(2)
U/Å^3	1 899(1)	1 099.2(4)
Z	8	2
D_c/g cm^{-3}	2.149	2.398
D_m/g cm^{-3}	2.19	2.56
μ/cm^{-1}	23.2	29.8
F(000)	1 200	760
Space group	$P2_1/n$	$P\bar{1}$
Data collection		
$2\theta_{max.}$/°	52	60
Collection range	*h*, −11 to +11; *k*, 0—16; *l*, 0—19	*h*, 0 to 14; *k*, −14 to +15; *l*, −14 to +14
Unique reflections measured	3 191	6 359
Crystal size/mm	0.42 × 0.36 × 0.30	0.26 × 0.22 × 0.20
Structure solution and refinement		
R	0.053	0.052
R′	0.059	0.056
w^b (A)	0.84	2.4
(B)	4.0×10^{-3}	3.1×10^{-4}
Data used	2 743	3 661
Discrimination	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$

[a] Crystal data for [{Ag($O_2CCH_2OC_6H_3Cl_2$-2,4)}$_n$] (**2**): $C_8H_5AgCl_2O_3$, $M = 327.9$, $a = 8.93(2)$, $b = 13.32(3)$, $c = 15.94(4)$ Å, $\beta = 97.7(1)°$, $U = 1\,880$ Å^3, $Z = 8$, $D_c = 2.31$, $D_m = 2.29$ g cm^{-3}. [b] $w = A/(\sigma^2 F_o + BF_o^2)$.

1. Intensity data for (**1**) and (**3**) were collected at 293 K on a Nicolet R3m four-circle diffractometer using graphite-monochromated Mo-K_α *X*-radiation (λ = 0.7107 Å). The data were corrected for absorption. Structures were solved by the Patterson method and refined by blocked-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms, using SHELX 76.[3] Hydrogen atoms were located by difference Fourier methods and were included in the refinement at fixed positions with the isotropic thermal parameters set invariant at $U = 0.05$ Å^2. Neutral-atom scattering factors were used[4] while heavy atoms were also corrected for anomalous dispersion.[4] Final atomic positional parameters are listed in Table 2 while interatomic distances and angles about the co-ordination spheres for (**1**) and (**2**) are given in Table 3.

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

Discussion

Complexes [{Ag($O_2CCH_2OC_6H_3$Me-2,Cl-4)}$_n$], (**1**), *and* [{Ag($O_2CCH_2OC_6H_3Cl_2$-2,4)}$_n$], (**2**).—Complex (**1**) is based on repeating linear AgO_2 units which are extended into a zig-zag polymer through the carboxylate oxygens of the phenoxyalkanoate ligand (Figure 1). There are two independent but similar silver centres in the asymmetric unit, each bonded to different carboxylate groups. [For (**1**), Ag(1)–O(11A), 2.217(3); Ag(1)–O(11B′), 2.210(3); Ag(2)–O(10A), 2.189(3); Ag(2)–O(10B), 2.185(3) Å; O(11A)–Ag(1)–O(11B′), 177.5(2); O(10A)–Ag(2)–O(10B), 176.8(2)°.] Because one linear silver bond is approximately 90° to the next, an *anti–syn* motif results, previously described for copper carboxylates[5] but not observed for silver(I) carboxylates. The *syn–syn* motif results in the more usual tetrakis(carboxylato-*O*,*O*′) bridged dimer for copper(II)[6] and the bis(carboxylato-*O*,*O*′) bridged dimer for silver(I).[2] Among the silver(I) phenoxyalkanoates, and with carboxylates generally, this motif is the only known type although linear systems, with two-co-ordinate silver, extended into polymers, are considered the more usual for silver(I).[7] Another analogous acid ligand, (phenylthio)ethanoate gives a complex, [{AgL}$_n$],[8] which does not fit the classification system.[2] This example is considered anomalous since the thioether S atom also co-ordinates with Ag, giving a five-membered chelate ring involving a bond to the carboxylate oxygen, with Ag having tetrahedral co-ordination. The other carboxylate oxygen then extends the complex into a three-dimensional polymer. In the silver(I) complexes with phenoxyalkanoates, the ether oxygens do not interact with the metal. However, there are some metal(II) examples in which this oxygen is also bonded (Cu^{II},[9] Zn^{II},[10] Pb^{II}[11]).

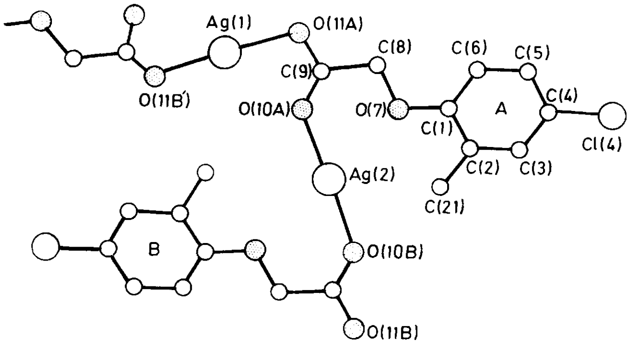

Figure 1. Molecular configuration and atom numbering scheme for [{Ag($O_2CCH_2OC_6H_3$Me-2,Cl-4)}$_n$], (**1**). Hydrogens are omitted for clarity

The isomorphous complex (**2**), has been characterised by chemical analysis (Found: C, 29.2; H, 1.50. Calc. for $C_8H_5AgCl_2O_3$, C, 29.3; H, 1.50%), single crystal and powder diffractometry (Table 1). The change from a methyl to a chloro substituent in the 2-position of the benzene ring has little influence upon the spatial requirements for the ligand molecules. Although this phenomenon is not unexpected, isomorphism has not been previously observed either in complexes with (4-chloro-2-methylphenoxy)ethanoate[12,13] or (2,4-dichlorophenoxy)ethanoate,[14,15] or for the corresponding acids (cmpe[16] and dcpe[17]). The acid cmpe is planar while dcpe has its side-chain synclinally related to the phenyl ring, with the torsion angle most sensitive to conformational change [C(1)–O(7)–C(8)–C(9)], either *ca.* 180° or *ca.* 90°; *e.g.* 174 (cmpe) and 80° (dcpe). Although dcpe has the synclinal conformation, this is considered to be the exception among both the phenoxyethanoic acids and the metal phenoxyethanoate complexes. With dcpe complexes, the ligand reverts to the preferred planar conformation, *e.g.* with [$ZnL_2(H_2O)_4$·$ZnL_2(H_2O)_2$], torsion angles are 172, 178, 176, and 178°;[13] for [K(L)·0·5H_2O], 172° [L = (2,4-dichlorophenoxy)ethanoate].[14] For complex (**1**), the two independent values are +177.2 (molecule A) and −171.6° (molecule B).

Packing of molecules of (**1**) in the unit cell (Figures 1 and 2) involves inter-chain interactions *via* carboxylate oxygens alone. However, stabilization of the chain structure is achieved through interactions between both carboxylate and ether oxygens and the silver ions [Ag(1)–O(10A), 2.72, Ag(1)–O(10B′), 2.75;

Table 2. Final atomic co-ordinates (× 10^4) for (**1**) and (**3**)

	Molecule A				Molecule B		
Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
(**1**) $[\{Ag(O_2CCH_2OC_6H_3Me\text{-}2,Cl\text{-}4\}_n]$							
Ag	1 184.6(5)	882.7(4)	4 555.6(3)	Ag	−1 370.4(6)	2 330.3(4)	2 005.1(3)
C(1)	−5 286(6)	1 108(4)	2 062(3)	C(1)	2 626(5)	3 518(4)	1 966(3)
C(2)	−5 638(6)	1 159(4)	1 153(3)	C(2)	3 723(6)	3 670(4)	1 477(3)
C(21)	−4 426(7)	1 283(6)	621(4)	C(21)	1 773(7)	3 316(6)	3 410(4)
C(3)	−7 142(6)	1 112(4)	768(3)	C(3)	5 220(6)	3 756(4)	1 869(4)
C(4)	−8 233(6)	993(4)	1 267(4)	C(4)	5 536(6)	3 682(4)	2 758(4)
Cl(4)	−10 113(2)	956(1)	766(1)	Cl(4)	7 426(2)	3 796(2)	3 265(1)
C(5)	−7 987(6)	918(4)	2 156(4)	C(5)	4 467(6)	3 542(4)	3 264(3)
C(6)	−6 399(6)	967(4)	2 548(4)	C(6)	2 963(6)	3 452(4)	2 866(3)
O(7)	−3 791(4)	1 193(3)	2 408(2)	O(7)	1 118(4)	3 426(3)	1 621(2)
C(8)	−3 416(6)	976(4)	3 308(3)	C(8)	732(6)	3 604(4)	713(3)
C(9)	−1 731(6)	1 047(4)	3 598(3)	C(9)	−944(6)	3 632(4)	440(3)
O(10)	−856(4)	1 350(3)	3 128(3)	O(10)	−1 828(4)	3 376(3)	929(3)
O(11)	−1 281(5)	766(3)	4 374(2)	O(11)	−1 368(4)	3 960(3)	−314(2)
(**3**) $[\{Ag_2(O_2CCH_2OC_6H_4Cl\text{-}2)_2\cdot AgClO_4\}_n]$							
Ag(1)	4 216.2(7)	8 764.0(5)	9 360.5(6)	Ag(2)	5 746.8(7)	6 492.1(6)	8 833.1(6)
C(1)	6 911(7)	11 392(8)	3 523(7)	C(1)	1 284(7)	6 010(7)	15 300(7)
C(2)	6 486(8)	12 691(7)	3 419(8)	C(2)	503(7)	6 913(9)	16 023(7)
Cl(2)	5 485(2)	13 223(2)	4 834(3)	Cl(2)	449(2)	8 486(2)	15 198(3)
C(3)	6 378(11)	13 497(9)	2 145(12)	C(3)	−167(8)	6 535(11)	17 382(9)
C(4)	7 699(13)	13 018(15)	1 017(10)	C(4)	−92(11)	5 333(14)	18 032(9)
C(5)	8 086(11)	11 605(14)	1 162(8)	C(5)	620(10)	4 409(9)	17 358(9)
C(6)	7 708(9)	10 931(10)	2 386(8)	C(6)	1 360(8)	4 735(8)	15 950(8)
O(7)	6 492(5)	10 635(4)	4 798(4)	O(7)	1 947(5)	6 489(4)	13 965(4)
C(8)	6 909(7)	9 303(6)	4 964(6)	C(8)	2 762(7)	5 639(6)	13 156(6)
C(9)	6 401(7)	8 670(6)	6 439(7)	C(9)	3 489(7)	6 417(6)	11 750(6)
O(10)	5 796(5)	9 362(4)	7 277(4)	O(10)	3 395(5)	7 604(4)	11 512(4)
O(11)	6 627(5)	7 504(4)	6 704(5)	O(11)	4 128(6)	5 763(4)	10 923(5)
				Ag(3)	6 481.0(8)	11 411.2(6)	6 898.7(6)
				Cl	2 867(2)	11 899(2)	9 250(2)
				O(1)*	3 633(8)	10 902(7)	9 849(7)
				O(2)*	2 754(8)	12 973(7)	9 785(7)
				O(3)*	1 547(9)	11 545(8)	9 419(8)
				O(4)*	3 623(10)	12 158(10)	7 869(11)

* Refined isotropically.

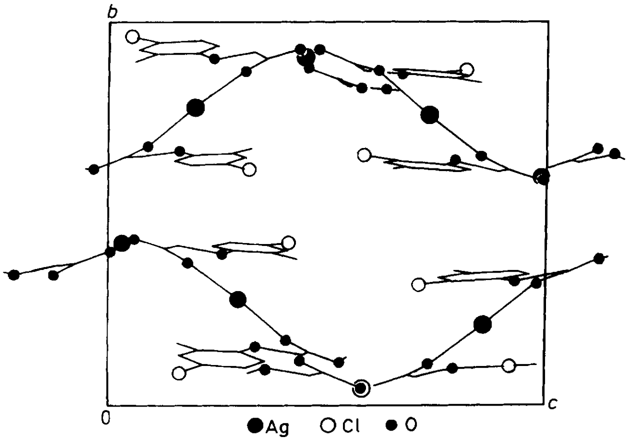

Figure 2. Packing of (**1**) in the unit cell

Ag(2)–O(7A), 2.85; Ag(2)–O(7B), 2.86 Å]. The atom Ag(1) is also involved in an inter-chain association with a carboxylate oxygen [Ag–O(11B′), 2.78 Å]. Intra-ligand O(7)–O(10) distances are 2.72 (A), 2.71 (B) compared to 2.62 Å in the parent acid.[16]

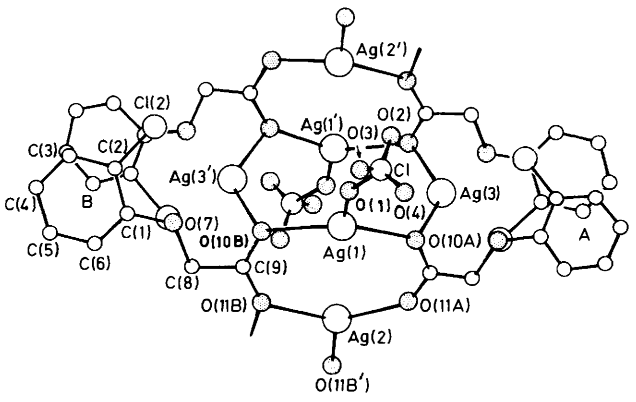

Figure 3. Molecular configuration and atom-numbering scheme for $[\{Ag_2(O_2CCH_2OC_6H_4Cl\text{-}2)_2\cdot AgClO_4\}_n]$, (**3**)

Complex $[\{Ag_2(O_2CCH_2OC_6H_4Cl\text{-}2)_2\cdot AgClO_4\}_n]$, (**3**).—Complex (**3**) is a polymer based on a bis(carboxylato-*O*,*O*′) bridged $[Ag_2L_2]$ dimer (Figure 3), with a Ag–Ag distance of 2.809(1) Å. The intra-dimer Ag–O distances and O–Ag–O angles are 2.229—2.373(4) Å and 156.2(2), 159.9(2)° respectively. The dimers are extended into the polymer structure (Figure 4)

Table 3. Bond distances (Å) and angles (°) for complexes (**1**) and (**3**) (co-ordination spheres only)

(**1**)		(**3**)	
Ag(1)–O(11A)	2.217(3)	Ag(1)–O(10A)	2.258(4)
Ag(1)–O(11B′)	2.210(3)	Ag(1)–O(10B)	2.284(4)
Ag(2)–O(10A)	2.189(3)	Ag(1)–O(1)	2.454(4)
Ag(2)–O(10B)	2.185(3)	Ag(2)–O(11A)	2.229(4)
		Ag(2)–O(11B)	2.299(4)
		Ag(2)–O(11B′)	2.373(4)
		Ag(1)–Ag(2)	2.809(1)
		Ag(3)–O(10A)	2.296(4)
		Ag(3)–O(10B′)	2.322(4)
O(11A)–Ag(1)–O(11B′)	177.5(2)	O(10B)–Ag(1)–O(10A)	156.2(2)
O(10A)–Ag(2)–O(10B)	176.8(2)	O(10B)–Ag(1)–O(1)	97.4(2)
Ag(1)–O(11A)–C(9A)	104.5(3)	O(10A)–Ag(1)–O(1)	97.5(2)
Ag(1′)–O(11B)–C(9B)	104.9(3)	O(11A)–Ag(2)–O(11B)	159.9(2)
Ag(2)–O(10B)–C(9B)	126.6(3)	O(11A)–Ag(2)–O(11B′)	111.5(2)
Ag(2)–O(10A)–C(9A)	127.4(3)	O(11B)–Ag(2)–O(11B′)	76.3(2)
		Ag(1)–O(10B)–C(9B)	120.0(4)
		Ag(1)–O(10A)–C(9A)	127.9(4)
		Ag(1)–O(10A)–Ag(3)	110.6(2)
		Ag(3)–O(10A)–C(9A)	121.0(4)
		Ag(1)–O(1)–Cl	125.6(6)
		Ag(2)–O(11A)–C(9A)	117.0(4)
		Ag(2)–O(11B)–C(9B)	126.0(4)
		O(10A)–Ag(3)–O(10B′)	126.4(4)

Symmetry operation for Ag(1′) is $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

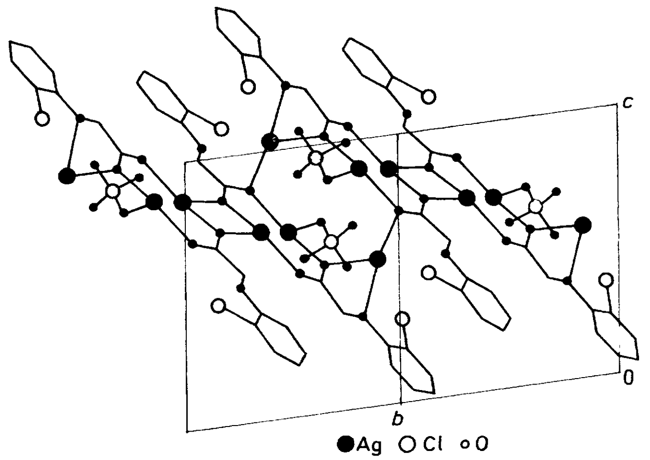

Figure 4. Packing of (**3**) in the unit cell

via two bridge types. The first involves a carboxylate oxygen, O(11B′) [Ag(2)–O(11B′), 2.373(4) Å], through the axial site of the dimer, giving a type D structure.[2] The second link is through the third silver ion [Ag(3)] which has two-co-ordinate angular stereochemistry [Ag–O(10B′), 2.322(4); Ag–O(10A), 2.296(4) Å; O–Ag–O, 126.4(4)°]. The atom Ag(3) also has longer stabilizing contacts with O(7A) [2.660(5) Å], O(7B′) [2.708(4) Å], and a perchlorate oxygen, O(4) [2.809(6) Å]. In addition, there is a longer contact to Cl(2A) [3.006(3) Å]. Complex (**3**) therefore represents the closest approach to the chelate mode found among the silver(I) phenoxyalkanoates. In the analogous chelate system in the copper(II) phenoxyalkanoates, the Cu–O (ether) distance is typically 2.41—2.48 Å and occupies the tetragonally distorted octahedral site.[9]

Another unusual feature of the complex is the co-ordinated perchlorate in the second axial site of the dimer [Ag(1)–O(1), 2.454(4) Å; O–Ag–O, 97.5(2), 97.4(2)°]. In both respects, this complex represents a unique example among silver(I) carboxylates. Whereas the occcurrence of both perchlorate and nitrate anions bound to Ag is common, particularly with adducted neutral organic molecules, axially bound perchlorates in silver carboxylates are unknown. Even in the somewhat analogous type D complex, silver(I) glycine nitrate $[\{Ag_2(O_2CCH_2NH_3)_2\}_n][NO_3]_{2n}$, where a nitrate is found in one of the axial sites, the Ag–O distance (2.89 Å)[18] is considerably longer than in complex (**3**). The (2-chlorophenoxy)ethanoate ligands in complex (**3**) are essentially planar [torsion angle C(1)–O(7)–C(8)–C(9), +177.2 (molecule A), −175.0° (molecule B)], which is also the conformation of the parent acid (equivalent angle, 180°).[19] Similarly, the interactive O(ether)···O(carboxyl) distance in the ligand side-chain is not significantly changed compared to that of the parent acid (2.609, 2.613 Å, *cf.* 2.640 Å). This is essentially the observation for complexes of (2-chlorophenoxy)ethanoic acid,[20] which generally behaves atypically compared to complexes of other phenoxyalkanoic acids. It is evident that the 2-chloro substituent in the ring system exerts a greater influence upon the stereochemistry of the complex formed than other 2-substituents, *e.g.*, –F, –CHO, $-CONH_2$, $-CH_3$, $-NO_2$.

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