Metal–Phenoxyalkanoic Acid Interactions. Part 13.[1] Copper(II)–(2-Chlorophenoxy)ethanoic Acid Complexes. Crystal and Molecular Structures† of *catena*-Tetra-μ-[(2-chlorophenoxy)ethanoato-*O,O′*]-dicopper(II), *catena*-(2-Aminopyrimidine-*N,N′*)-tetra-μ-[(2-chlorophenoxy)ethanoato-*O,O′*]-dicopper(II), and 1,2,2,2,2-Penta-aqua-tetra-μ-[(2-chlorophenoxy)-ethanoato-*O,O′*]-copper(II)calcium(II)

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The crystal structures of three copper(II) complexes of (2-chlorophenoxy)ethanoic acid have been determined by *X*-ray diffraction. Anhydrous $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4\}_n]$ (**1**) is monoclinic, a = 11.587(3), b = 5.084(2), c = 29.600(6) Å, β = 103.76(2)°, Z = 2, space group $P2_1/c$. The adduct $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4(ampym)\}_n]$ (ampym = 2-aminopyrimidine) (**2**) is triclinic, a = 17.543(5), b = 13.344(5), c = 8.459(3) Å, α = 77.89(3), β = 81.43(3)°, γ = 87.61(3)°, Z = 2, space group $P\bar{1}$. $[CaCu(O_2CCH_2OC_6H_4Cl\text{-}2)_4(H_2O)_5]$ (**3**) is orthorhombic, a = 13.800(4), b = 8.426(3), c = 32.558(10) Å, Z = 4, space group $C222_1$. (**1**), (**2**), and (**3**) were refined to residuals of 0.051, 0.060, and 0.046 for 1 752, 3 399, and 1 042 observed reflections respectively. All three complexes have tetracarboxylate bridged dimer systems [Cu–Cu, 2.583(2) Å (**1**); 2.700(3), 2.730(3) Å (**2**); and Ca–Cu, 3.480(3) Å (**3**)]. In both (**1**) and (**2**), the centrosymmetric dimer units are extended into polymer structures *via* axial groups which in (**1**) are carboxyl oxygens from adjacent dimer units while in (**2**) they are the *meta*-related nitrogens of the pyrimidine rings. Complex (**3**) is monomeric with 'half' the dimer comprising a conventional $CuO_4(OH_2)$ unit, the other 'half' being an eight-co-ordinate $CaO_4(OH_2)_4$ unit, with two-fold rotational symmetry.

Structural studies of the divalent metal complexes of the phenoxyalkanoic acids, which include the commercial auxin herbicides (2,4-dichlorophenoxy)ethanoic acid, (2,4,5-trichlorophenoxy)ethanoic acid, and (4-chloro-2-methylphenoxy)ethanoic acid have revealed a diversity of complexing modes and stereochemistries.[1–5] Although monomeric species predominate among the copper(II) complexes of these acids, three tetracarboxylate bridged dimers are known, $[Cu_2(O_2CCH_2OC_6H_3Cl_2\text{-}2,4)_4(H_2O)_2]\cdot 2H_2O$,[4] $[Cu_2(O_2CCH_2OC_6H_3Cl_2\text{-}2,4)_4(diox)_2]\cdot 0.5diox$ (diox = 1,4-dioxane),[5] and $[Cu_2(O_2CCH_2OC_6H_2Cl_3\text{-}2,4,5)_4(py)_2]$ (py = pyridine).[4] A variable-temperature magnetic moment study of anhydrous copper(II) (2-chlorophenoxy)ethanoate, $Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4$ (**1**), gave a value (1.50 B.M. at 298 K) indicative of a binuclear structure but the temperature dependence of the magnetic susceptibility [1.23 B.M. (196 K); 0.75 B.M. (77 K)] 'was not consistent with a binuclear structure'.[6] Unusual thermal properties are also associated with the solid-state chemistry of this compound. A second modification, a pale blue non-crystalline form (**1a**), undergoes a complete reversible solid-state change over the period of a few days into the dark green anhydrous form when left in contact with the aqueous alcoholic mother-liquor. The polymorph (**1a**) has been analysed as a tetrahydrate, $[Cu(O_2CCH_2OC_6H_4Cl\text{-}2)_2(H_2O)_4]$. Infrared and visible spectroscopy and differential thermal–thermogravimetric analyses indicate that this form is a monomeric six-co-ordinate species. Treatment of either complexes (**1**) or (**1a**) with pyridine in aqueous ethanol yields a dark blue adduct (**1b**) with an elemental analysis and properties suggestive of a five-co-ordinate species $[Cu(O_2CCH_2OC_6H_4Cl\text{-}2)_2(py)_2(H_2O)]$, possibly similar to aquabis(phenoxyethanoato)bis(pyridine)-copper(II)[7] and aquabis[(4-chloro-2-methylphenoxy)ethanoato]bis(pyridine)copper(II).[8] However, uncompromising crystal twinning characteristics obviated a structure analysis *via* single-crystal *X*-ray diffraction although accurate lattice parameters were determined. Greater success was achieved with adduct formation using 2-aminopyrimidine (ampym) which yielded dark green crystals of a complex (**2**) having no tendency to form twins. Furthermore, elemental analysis and single-crystal *X*-ray preliminaries suggested the possibility of a tetracarboxylate bridged dimer species of the copper(II) ethanoate hydrate type[9] [stoicheiometry: $Cu(O_2CCH_2OC_6H_4Cl\text{-}2)_2(ampym)_{0.5}$; space group $P\bar{1}$ with four formula units per cell].

A product obtained in low yield in the preparative route with neutral ammonium (2-chlorophenoxy)ethanoate and copper(II) ethanoate in aqueous medium [after removal of the bulk of the (**1a**) product] is exclusively a pale blue crystalline form (**3**) which is stable to reversion to (**1**). Because of the small amount of product obtained for (**3**), no elemental analysis was carried out. Initially this complex was thought to be a $[\{Cu(O_2CCH_2OC_6H_4Cl\text{-}2)_2(H_2O)\}_n]$ polymer. However the *X*-ray structure determination has confirmed the presence of a tetracarboxylate bridged Ca–Cu species $[CaCu(O_2CCH_2OC_6H_4Cl\text{-}2)_4(H_2O)_5]$. Compound (**3**) can also be prepared in quantity using equimolar amounts of calcium and copper(II) ethanoates by the

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† *Supplementary data available* (No. SUP 56064, 9 pp.): thermal parameters, ligand bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: B.M. = 0.927×10^{-23} A m^2.

general neutral salt method. The crystal structure determinations of the complexes (**1**), (**2**), and (**3**) have also provided some insight into the anomalous nature of the copper–(2-chlorophenoxy)ethanoic acid interaction. It is also of interest to compare the structural and conformational features of complexes *vs.* the uncomplexed (2-chlorophenoxy)ethanoic acid species since the structure of the free acid is known.[10]

Experimental

Preparation of Complexes.—$[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4\}_n]$ (**1**) was prepared by allowing the pale blue hydrated compound $[Cu(O_2CCH_2OC_6H_4Cl\text{-}2)_2(H_2O)_4]$ (**1a**) to remain in contact with the aqueous ethanolic mother-liquor for a period of several days. Compound (**1a**) precipitated almost immediately upon cooling the filtrate from the reaction of copper(II) carbonate with a boiling solution of (2-chlorophenoxy)ethanoic acid using the general procedure previously described.[11] The conversion of (**1a**) to (**1**) is total and may be reversed by simply re-heating the suspension in which both forms are insoluble. Removal of the mother-liquor, which invariably contains some unreacted (2-chlorophenoxy)ethanoic acid, and replacing it with either ethanol or water prevents the reversion. Crystals of (**1**) are inherently twinned but a specimen obtained by cleavage of the terminal cap of a chisel-shaped prismatic crystal proved to be less seriously affected and collection of *X*-ray data was possible [Found for (**1**): C, 44.0; H, 2.95; Cl, 16.2; Cu, 14.5. Calc. for $C_{16}H_{12}Cl_2CuO_6$: C, 44.2; H, 2.78; Cl, 16.3; Cu, 14.6%. Found for (**1a**): C, 37.9; H, 4.05; Cl, 13.9; Cu, 12.6. Calc. for $C_{16}H_{20}Cl_2CuO_{10}$: C, 37.9; H, 4.00; Cl, 14.0; Cu, 12.5%]. The complex $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4(ampym)\}_n]$ (**2**) was prepared in a similar manner to (**1b**) by treating an ethanolic suspension of (**1**) with an ethanolic solution of 2-aminopyrimidine [Found for (**2**): C, 44.9; H, 3.10; Cl, 14.5; Cu, 13.0. Calc. for $C_{36}H_{29}Cl_4Cu_2N_3O_{12}$: C, 44.8; H, 3.05; Cl, 14.7; Cu, 13.2%].

Crystals of $[CaCu(O_2CCH_2OC_6H_4Cl\text{-}2)_4(H_2O)_5]$ (**3**) were obtained by allowing the pale blue aqueous mother-liquor from the preparation of (**1**), by the neutral salt methods,* to evaporate partially at room temperature. Subsequent preparations by the same method but using stoicheiometric amounts of calcium and copper(II) ethanoate also gave crystalline (**3**) (confirmed by powder *X*-ray diffractometry and elemental analysis) (Found: C, 40.8; H, 3.70. Calc. for $C_{32}H_{34}CaCl_4CuO_{17}$: C, 41.1; H, 3.65%).

Crystal Data.—(**1**) $C_{32}H_{24}Cl_4Cu_2O_{12}$, $M = 869.4$, monoclinic, $a = 11.587(3)$, $b = 5.084(2)$, $c = 29.600(6)$ Å, $\beta = 103.76(2)°$, $U = 1\,693.6$ Å^3, $D_m = 1.70$, $D_c = 1.704$ g cm^{-3}, $Z = 2$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 16.8 cm^{-1}, $F(000) = 876$, space group $P2_1/c$ (C^5_{2h}, no. 14).

(**1b**) $C_{26}H_{24}Cl_2CuN_2O_7$, $M = 610.9$, orthorhombic, $a = 17.18(1)$, $b = 13.566(8)$, $c = 5.602(2)$ Å, $U = 1\,316.8$ Å^3, $D_m = 1.55$, $D_c = 1.540$ g cm^{-3}, $Z = 2$, $F(000) = 626$, space group *Pba*2.†

(**2**) $C_{36}H_{29}Cl_4Cu_2N_3O_{12}$, $M = 964.5$, triclinic, $a = 17.543(5)$, $b = 13.344(5)$, $c = 8.459(3)$ Å, $\alpha = 77.89(3)$, $\beta = 81.43(3)$, $\gamma = 87.61(3)°$, $U = 1\,914.6$ Å^3, $D_m = 1.68$, $D_c = 1.673$ g cm^{-3}, $Z = 2$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 15.0 cm^{-1}, $F(000) = 976$, space group $P\bar{1}$ (C_i^1, no. 2).

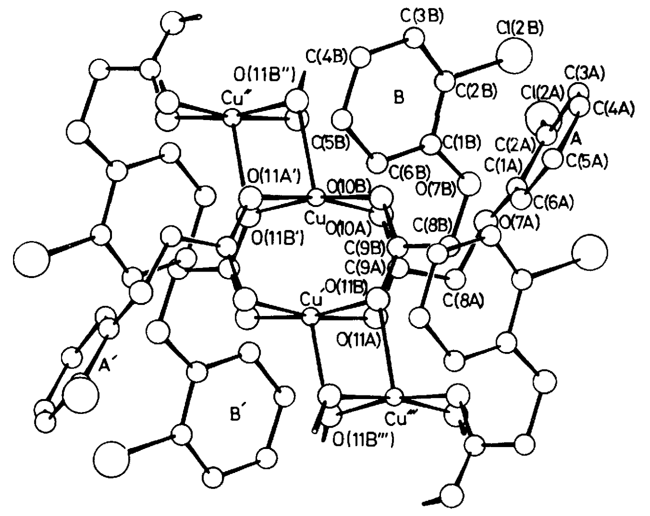

Figure 1. Molecular configuration and atom numbering scheme for $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4\}_n]$ (**1**). Primed atoms are generated by an inversion operation

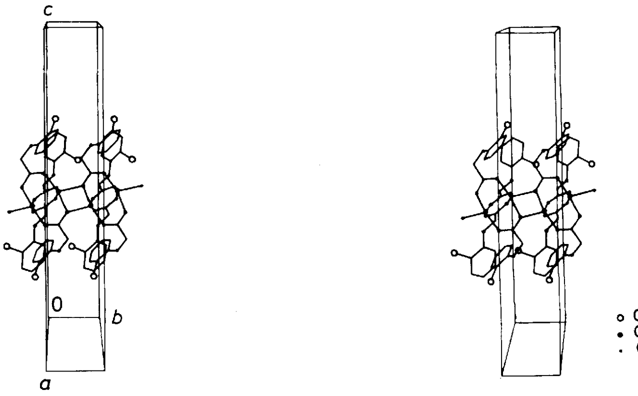

Figure 2. Stereoview of a portion of the polymeric structure of (**1**) extending down the *b* axis at *c ca.* $\frac{1}{2}$

(**3**) $C_{32}H_{34}CaCl_4CuO_{17}$, $M = 936.0$, orthorhombic, $a = 13.800(4)$, $b = 8.426(3)$, $c = 32.558(10)$ Å, $U = 3\,785.9$ Å^3, $D_m = 1.64$, $D_c = 1.642$ g cm^{-3}, $Z = 4$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 10.9 cm^{-1}, $F(000) = 1\,916$, space group $C222_1$ (D_2^5, no. 20).

Structure Solution and Refinement.—1 752, 3 399, and 1 042 reflections with $I > 2.5\sigma(I)$ were considered observed out of 2 592 (**1**), 5 197 (**2**), and 1 492 (**3**) collected in unique sets ($2\theta_{max.} = 50°$; graphite-monochromatized Mo-K_α radiation) on a Syntex P2$_1$ four-circle diffractometer. Crystal sizes were 0.24 × 0.26 × 0.06 (**1**), 0.32 × 0.20 × 0.20 (**2**), and 0.10 × 0.30 × 0.28 mm (**3**). The structures were solved by heavy-atom and Fourier

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* In the neutral salt method, the ammonium salt of (2-chlorophenoxy)ethanoic acid is formed by treating a hot aqueous suspension of the acid with dilute ammonia solution. This solution is then taken to incipient dryness on a steam-bath to remove excess ammonia, after which the solids are re-dissolved in water and an aqueous solution of copper(II) ethanoate added (solution pH = 5.4). Upon cooling, the bulky precipitate of (**1a**) forms. It appears that only a trace of Ca^{2+} is necessary to form the double 'salt' since in the initial preparation, no Ca^{2+} was added. It can only be assumed that in this instance, it was scavenged from the reagents or the water.

† From systematic absences (0*kl* absent for *k* = odd; *h*0*l* absent for *h* = odd) both space groups *Pba*2 and *Pbam* are possible. However, for *Z* = 2, the centrosymmetric space group is precluded since it requires 2/*m* molecular symmetry, whereas *Pba*2 only requires that the molecular symmetry is coincident with the crystallographic two-fold symmetry, as is found in the five-co-ordinate square pyramidal complexes; $[Cu(O_2CCH_2OPh)_2(py)_2(H_2O)]$[7] and $[Cu(O_2CCH_2OC_6H_3MeCl\text{-}2,4)_2(py)_2(H_2O)]$.[8]

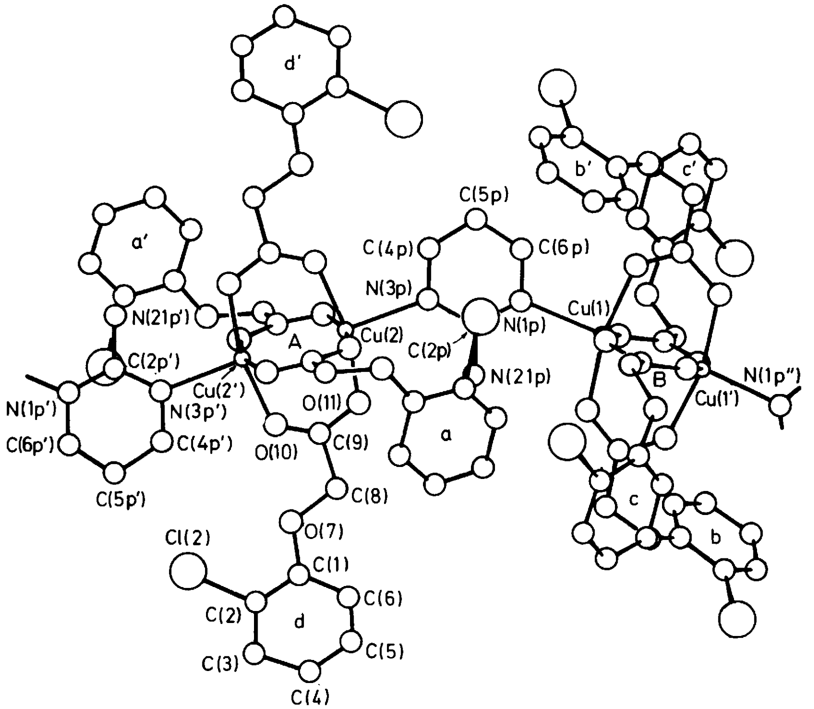

Figure 3. Molecular configuration and atom numbering scheme for $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4(ampym)\}_n]$ (2) showing the two independent dimeric species (A and B) in the asymmetric unit. Primed atoms are generated by an inversion operation

methods and refined by blocked-matrix least squares with anisotropic thermal parameters for all non-hydrogens to final R values $[=\Sigma\|F_o| - |F_c\|/\Sigma|F_o|]$ of 0.051 (1), 0.060 (2), and 0.046 (3). Unit weights were used for (1) while weighting schemes of the type $w = 1.00/(\sigma^2F_o + 0.0004\ F_o^2)$ (2) and $1.33/(\sigma^2F_o + 0.0003\ F_o^2)$ (3) gave weighted residuals $[R' = (\Sigma w\|F_o - F_c\|^2/\Sigma w|F_o^2)^{\frac{1}{2}}]$ of 0.066 (2) and 0.044 (3).

It was found that for compound (2), some of the atoms of the ring system of ligand D [C(1), C(2), C(3), and C(6)] and of the pyrimidine ring [C(5p), and C(6p)] were disordered. These atoms were subsequently refined over two sites with site occupancy factors fixed at 0.5, the ligand atoms anisotropic and the pyrimidine atoms isotropic. Hydrogen atoms were located by difference-Fourier synthesis and included in the refinement at fixed positions with their isotropic thermal parameters also fixed ($U = 0.05$ Å^2). No corrections were made for either absorption or extinction. Neutral-atom scattering factors were used[12] while metal and chlorine atoms were corrected for the effects of anomalous dispersion.[12] All computations were completed using the SHELX 76 program set.[13]

Final atomic positional parameters are listed in Table 1 while interatomic distances and angles about the co-ordination spheres for (1), (2) and (3) are given in Table 2.

Discussion

The structure of $[Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4\}_n]$ (1) consists of centrosymmetric tetracarboxylate bridged dimers of the copper(II) ethanoate hydrate type[9] but with the axial water ligands absent and replaced by the oxygens of adjacent carboxyl groups. This extends the structure into a polymer motif (Figures 1 and 2), in a manner similar to that found in the anhydrous forms of copper(II) propanoate[14] and copper(II) butanoate.[15] The structural parameters for the tetracarboxylate cage for (1) are also comparable: Cu–Cu, mean Cu–O (equatorial), and Cu–O (axial) distances being 2.583(2), 1.965(5), 2.169(5); 2.578(4), 1.94(1), 2.28(1); and 2.565, 1.982, 2.245 Å respectively for (1), copper(II) propanoate, and copper(II) butanoate. The Cu–O-(axial) distance in (1) is somewhat contracted compared with the other examples and represents a stronger bonded polymer (consistent with the nature of this compound) but is not abnormally short when the range of distances for known binuclear copper(II) carboxylates is reviewed.[16,17] Among the 43 examples * in ref. 17, the Cu–Cu distances range from 2.563 Å in $[Cu_2(O_2CEt)_4(diox)]$[22] to 2.886 Å $[Cu_2(O_2CCF_3)_4(quin)]$[23] (quin = quinoline) so that the anhydrous complexes represent some of the shortest known, although there is no correlation between this distance and the nature of axial group. A direct relationship does exist between the Cu–Cu separation and the Cu to basal plane distance.[17] .This means that the Cu–Cu variation is accommodated by a flexing of the Cu atoms out of the basal plane, with the actual separation of the least-squares planes to the two CuO_4 moieties remaining relatively constant. The Cu–O(axial) distance remains relatively constant throughout the series. However, the apical ligands do play a part in determining the magnetic $2J$ value for this series, increasing as the ligands become stronger electron donors,[17] whereas this value is insensitive to the Cu–Cu distance.

In the structure of $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4(ampym)\}_n]$ (2), two crystallographically independent tetracarboxylate dimers (A and B) exist, with Cu–Cu separations of 2.730(3) and 2.700(3) Å respectively (Figure 3). The mean Cu–O(equatorial)

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* An additional seven examples of binuclear copper(II) carboxylates are now known. These, with their Cu–Cu separations are: $[Cu_2(O_2CCH_2OC_6H_3Cl_2\text{-}2,4)_4(H_2O)_2]\cdot 2H_2O$, 2.639(5) Å;[5] $[Cu_2(O_2CCH_2OC_6H_2Cl_3\text{-}2,4,5)_4(py)_2]$, 2.716(7) Å;[5] $[Cu_2(O_2CCH_2SPh)_4(py)_2]$, 2.646(1) Å;[18] $[Cu_2(O_2CCH_2SC_6H_2Cl_2Me\text{-}2,4,5)_4(Me_2CO)_2]$, 2.646(1) Å;[18] $[Cu_2\{C_8H_{15}NOCO_2\}_4(EtOH)_2]$, 2.644 Å;[19] $[Cu_2\{O_2CCH_2NHC(O)Me\}_4(H_2O)_2]$, 2.666(1) Å;[20] and $[Cu_2(O_2CCH_2OC_6H_4F\text{-}4)_4(ampym)_2]$, 2.710(1) Å.[21]

Table 1. Atomic co-ordinates ($\times 10^4$) for $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4\}_n]$ (**1**), $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4(ampym)\}_n]$ (**2**), and $[CaCu(O_2CCH_2OC_6H_4Cl\text{-}2)_4(H_2O)_5]$ (**3**)

(*a*) Complex (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	−138(1)	7 172(2)	−233(1)			
	Ligand A			Ligand B		
C(1)	3 316(7)	6 531(18)	−823(3)	2 087(8)	5 956(16)	1 752(3)
C(2)	3 781(8)	8 400(18)	−1 071(3)	2 183(8)	3 957(17)	2 080(3)
Cl(2)	4 955(2)	10 341(6)	−788(1)	956(2)	3 228(5)	2 302(1)
C(3)	3 331(10)	8 672(22)	−1 557(3)	3 206(7)	2 602(19)	2 242(3)
C(4)	2 412(11)	7 071(28)	−1 774(3)	4 170(8)	3 144(21)	2 047(4)
C(5)	1 978(9)	5 157(24)	−1 533(4)	4 094(3)	5 068(23)	1 710(4)
C(6)	2 415(8)	4 874(20)	−1 059(3)	3 036(8)	6 460(20)	1 559(3)
O(7)	3 790(5)	6 471(13)	−349(2)	1 021(5)	7 623(11)	1 640(2)
C(8)	3 389(7)	4 520(19)	−80(3)	765(8)	8 919(16)	1 241(3)
C(9)	2 128(6)	4 904(16)	−30(2)	505(6)	7 329(15)	792(2)
O(10)	1 550(4)	6 860(12)	−210(2)	499(5)	4 920(10)	805(2)
O(11)	1 773(4)	3 099(12)	195(2)	273(4)	8 692(9)	418(2)
H(3)	3 404	9 978	−1 758	3 417	1 162	2 553
H(4)	2 035	6 836	−2 138	4 997	1 907	2 141
H(5)	1 220	3 858	−1 676	4 694	5 501	1 498
H(6)	2 235	3 113	−855	3 076	7 840	1 384
H(81)	3 797	4 951	182	1 375	9 990	1 269
H(82)	3 454	2 678	−200	111	9 715	1 237

(*b*) Complex (**3**)

Cu	−3(1)	0	0	H(1w)	1 950	420	120
Ca	−2 524(2)	0	0	H(21w)	−3 740	−1 290	−340
O(1w)	1 641(7)	0	0	H(22w)	−4 000	−2 330	−510
O(2w)	−3 240(6)	−2 012(10)	−461(3)	H(31w)	−3 780	−2 400	510
O(3w)	−3 615(8)	−1 362(9)	457(3)	H(32w)	−3 860	−810	610

	Ligand A			Ligand B		
C(1)	−389(9)	−3 485(13)	1 240(4)	−1 811(9)	−3 287(15)	−1 606(4)
C(2)	261(8)	−3 687(13)	1 566(4)	−2 597(9)	−4 278(16)	−1 653(4)
Cl(2)	1 236(2)	−4 997(6)	1 503(9)	−3 328(2)	−4 700(5)	−1 234(1)
C(3)	137(11)	−2 876(17)	1 930(3)	−2 820(4)	−4 981(22)	−2 029(4)
C(4)	−642(10)	−1 864(18)	1 981(4)	−2 194(12)	−4 642(2)	−2 365(4)
C(5)	−1 265(11)	−1 664(16)	1 664(4)	−1 402(13)	−3 700(18)	−2 325(4)
C(6)	−1 137(10)	−2 431(14)	1 289(4)	−1 180(12)	−2 944(18)	−1 948(4)
O(7)	−202(5)	−4 372(8)	895(2)	−1 678(7)	−2 577(10)	−1 227(2)
C(8)	−879(8)	−4 345(13)	565(4)	−765(8)	−1 910(15)	−1 142(3)
C(9)	−915(9)	−2 800(12)	317(3)	−809(10)	−1 159(12)	−717(3)
O(10)	−1 651(6)	−2 499(8)	122(2)	−1 574(5)	−456(8)	−613(2)
O(11)	−125(6)	−1 996(9)	324(2)	−26(7)	−1 194(8)	−518(2)
H(3)	660	−3 600	2 130	−3 280	−6 250	−2 090
H(4)	*a*			−2 290	−5 450	−2 610
H(5)	−2 030	−810	1 800	−980	−3 300	−2 620
H(6)	*a*			*a*		
H(81)	−1 210	−5 710	620	−180	−2 670	−1 130
H(82)	−1 730	−4 620	740	−510	−1 070	−1 330

(*c*) Complex (**2**)

Cu(1)	9 292(1)	9 761(1)	−4 111(2)	C(6p)	8 076(10)	8 121(14)[b]	−3 017(21)
Cu(2)	5 726(1)	9 677(1)	−433(2)	N(2p)	7 623(5)	10 446(8)	−1 761(13)
N(1p)	8 143(5)	9 108(7)	−2 897(12)	H(4p)	6 280	7 740	−1 330
C(2p)	7 540(6)	9 525(9)	−2 080(14)	H(5p)	*a*		
N(3p)	6 856(5)	9 064(7)	−1 498(12)	H(6p)	8 480	7 990	−4 330
C(4p)	6 784(7)	8 114(10)	−1 747(19)	H(21p)	8 090	10 860	−2 250
C(5p)	7 398(11)	7 550(15)	−2 378(24)[b]	H(22p)	7 210	10 820	−1 110

	Ligand A			Ligand B		
C(1)	3 878(8)	8 212(11)	5 471(16)	10 986(8)	13 163(11)	−3 802(18)
C(2)	3 138(9)	8 573(12)	5 822(17)	11 646(10)	13 739(12)	−4 392(19)

Table 1 (*continued*)

Atom	X/a	Y/b	Z/c	X/a	Y/b	Z/c
Cl(2)	3 000(2)	9 731(4)	6 434(6)	11 639(3)	14 753(3)	−6 044(6)
C(3)	2 500(9)	8 027(15)	5 675(20)	12 316(10)	13 509(16)	−3 668(25)
C(4)	2 603(9)	7 123(13)	5 168(21)	12 333(10)	12 672(18)	−2 350(27)
C(5)	3 344(11)	6 750(13)	4 795(23)	11 673(11)	12 123(15)	−1 761(21)
C(6)	3 980(9)	7 285(13)	4 938(21)	11 006(9)	12 352(13)	−2 471(19)
O(7)	4 477(5)	8 770(7)	5 709(10)	10 364(5)	13 425(5)	−4 591(11)
C(8)	5 195(7)	8 721(10)	4 682(16)	9 685(7)	12 841(10)	−4 048(16)
C(9)	5 144(8)	9 194(10)	2 888(17)	9 751(7)	11 767(10)	−4 413(15)
O(10)	4 524(5)	9 639(7)	2 591(10)	10 340(5)	11 550(6)	−5 282(10)
O(11)	5 717(5)	9 062(6)	1 900(10)	9 181(5)	11 195(6)	−3 793(11)
H(3)	2 020	8 440	6 160	12 790	13 960	−4 460
H(4)	2 040	6 640	5 110	13 020	12 780	−2 090
H(5)	3 280	6 080	4 240	11 750	11 260	−860
H(6)	4 520	6 800	4 920	10 450	11 960	−1 860
H(81)	5 400	7 990	4 710	9 530	12 760	−2 890
H(82)	5 450	9 170	5 330	9 330	13 140	−4 600
		Ligand C			Ligand D	
C(1)	10 753(9)	7 316(11)	−477(16)	4 467(10)	5 841(12)	−1 491(20)^{b}
C(2)	11 393(9)	6 703(11)	−178(19)	5 026(10)	5 375(13)	−2 418(21)^{b}
Cl(2)	12 068(2)	7 091(3)	855(6)	5 876(2)	5 937(3)	−3 348(5)
C(3)	11 492(10)	5 787(13)	−673(23)	4 927(8)	4 455(11)	−2 806(19)^{b}
C(4)	10 937(14)	5 461(16)	−1 475(24)	4 198(10)	4 100(15)	−2 066(21)
C(5)	10 289(14)	6 053(17)	−1 726(22)	3 626(11)	4 609(15)	−1 107(24)
C(6)	10 188(10)	6 992(14)	−1 252(20)	3 758(6)	5 415(8)	−832(13)^{b}
O(7)	10 628(5)	8 203(7)	139(10)	4 683(4)	6 802(6)	−1 336(11)
C(8)	10 972(7)	9 106(10)	−900(16)	4 105(7)	7 371(9)	−497(16)
C(9)	10 573(8)	9 459(9)	−2 381(16)	4 435(8)	8 381(9)	−357(14)
O(10)	9 854(5)	9 434(6)	−2 222(10)	5 138(5)	8 487(6)	−601(10)
O(11)	11 004(5)	9 783(6)	−3 694(10)	3 929(4)	8 999(6)	118(10)
H(3)	11 960	5 300	−230	*a*		
H(4)	11 060	5 150	−2 810	4 130	3 180	−2 190
H(5)	9 800	5 930	−2 210	*a*		
H(6)	9 660	7 510	−1 470	*a*		
H(81)	11 540	8 940	−1 230	3 920	6 890	720
H(82)	10 850	9 690	20	3 750	7 500	−1 210

		Ligand D (disordered atoms)				Pyrimidine ring (disordered atoms)	
C(1)	5 259(11)	6 302(17)	−544(26)^{b}	C(5p)	7 292(15)	7 802(20)	−3 129(32)^{b}
C(2)	5 851(13)	5 817(16)	−1 447(26)^{b}	C(6p)	7 947(19)	8 382(25)	−3 649(40)^{b}
C(3)	6 410(12)	5 226(16)	−602(25)^{b}				
C(6)	5 307(11)	6 304(11)	1 131(21)^{b}				

[a] Hydrogen atom not located. [b] Atom refined with site occupancy factor fixed at 0.5.

distances for the two dimers are 1.975(9), 1.969(9) Å while the C–N(axial) distances are 2.243(9) and 2.248(10) Å. These Cu–N(axial) distances are slightly longer than the distance found in [$Cu_2(O_2CCH_2OC_6H_2Cl_3$-2,4,5$)_4(py)_2$] [2.14(1) Å] but are within the series range (2.08—2.27 Å). The prime difference between (**2**) and the majority of the copper(II) dimers is that (**2**) is polymeric. The 2-aminopyrimidine ligands extend the dimers into linear polymer chains *via* the heteronitrogen atoms of the pyrimidine ring (both atoms 1 and 3). The *meta*-relation of these nitrogens means that dimers A and B are oriented at *ca.* 120° to one another in a one-dimensional polymer which extends along the *a* axis of the cell (Figure 4). These chains are not involved in any inter-chain hydrogen bonding associations *via* the 2-amino-group of the pyrimidine, but such inter-dimer associations are uncommon among copper(II) dimer systems. The bond distances and angles within the 2-aminopyrimidine ligand itself show little change compared with those of the free base.[24]

The 'mixed' calcium–copper compound [$CaCu(O_2CCH_2OC_6H_4Cl$-2$)_4(H_2O)_5$] (**3**) is discretely dimeric consisting of 'half' a conventional tetracarboxylate bridged copper(II) dimer, with four carboxyl oxygens in a square plane [mean Cu–O, 1.978(7) Å] and an axial water molecule [Cu–O, 2.269(10) Å]. The other 'half' of the dimer is an eight-co-ordinate $CaO_4(OH_2)_4$ unit with regular square antiprismatic stereochemistry about Ca [Ca–O, 2.407(10)—2.470(8) Å; mean 2.439(8) Å] (Figure 5). The complex has two-fold rotational symmetry coincident with a crystallographic two-fold axis at $y = z = 0$. The overall stereochemistry is square antiprismatic and differs markedly from the only other known example of a mixed calcium–copper complex, calcium copper ethanoate hexahydrate[25] (which is isomorphous with its Ca–Cd polymorph). The ethanoate has a polymer structure, with two bidentate carboxylates bridging alternately an octahedral six-co-ordinate $CaO_4(OH_2)_2$ centre and a tetrahedrally distorted square planar CuO_4 centre. With (**3**) the Ca–Cu distance is 3.480(3) Å [*cf.* 4.060(1) Å for the ethanoate analogue], which represents considerable elongation of the distance found in the Cu–Cu dimers and is a direct consequence of the larger (Ca–O) bond distances and the steric requirements of the CaO_8 square antiprism. This forces the Cu of the CuO_5 square prism below the basal plane of the square pyramid. No significant hydrogen-bonding associations are in evidence in the packing of the dimers in the unit cell (Figure 6).

The structural and conformational aspects of the (2-chloro-

Table 2. Bond distances (Å) and angles (°) about the co-ordination spheres for complexes (**1**)—(**3**)

[{Cu$_2$(O$_2$CCH$_2$OC$_6$H$_4$Cl-2)$_4$}$_n$] (**1**)

Cu–O(10A)	1.947(5)	Cu–O(11B)	2.024(5)
Cu′–O(11A)	1.929(5)	Cu–O(11B″)	2.169(5)
Cu′–O(10B)	1.960(5)	Cu–Cu′	2.583(2)
O(11B′)–Cu–O(10A)	94.1(2)	O(11A)–Cu–O(11B′)	169.5(2)
O(11B′)–Cu–O(11A)	89.5(2)	O(11B)–Cu–Cu′	81.2(2)
O(11B′)–Cu–O(10B)	108.7(2)	Cu–O(11B)–Cu′	137.0(4)
O(11B′)–Cu–O(11B)	81.8(2)	C(9A)–O(10A)–Cu	122.1(5)
O(10A)–Cu–O(11A)	169.8(2)	C(9A)–O(11A)–Cu	122.1(5)
O(10A)–Cu–O(10B)	90.0(2)	C(9B)–O(10B)–Cu	121.2(5)
O(10A)–Cu–O(11B)	89.1(2)	C(9B)–O(11B)–Cu	124.8(5)

[{Cu$_2$(O$_2$CCH$_2$OC$_6$H$_4$Cl-2)$_4$(ampym)}$_n$] (**2**)

Cu(1)–O(10B′)	1.981(8)	Cu(2)–O(10A′)	1.970(9)
Cu(1)–O(10C)	1.964(8)	Cu(2)–O(10D)	1.970(8)
Cu(1)–O(11B)	1.985(9)	Cu(2)–O(11A)	1.965(9)
Cu(1)–O(11C′)	1.968(9)	Cu(2)–O(11D′)	1.973(8)
Cu(1)–N(1p)	2.243(9)	Cu(2)–N(3p)	2.248(10)
Cu(1)–Cu(1′)	2.730(3)	Cu(2)–Cu(2′)	2.700(3)
N(1p)–Cu(1)–O(10B)	92.7(5)	N(3p)–Cu(2)–O(11A)	100.4(6)
N(1p)–Cu(1)–O(10C)	98.9(5)	N(3p)–Cu(2)–O(10D)	93.8(5)
N(1p)–Cu(1)–O(11B′)	101.6(6)	N(3p)–Cu(2)–O(10A′)	92.9(5)
N(1p)–Cu(1)–O(11C′)	96.2(5)	N(3p)–Cu(2)–O(11D′)	99.6(5)
O(11B)–Cu(1)–O(10C)	89.5(5)	O(11A)–Cu(2)–O(10D)	88.0(5)
O(11B)–Cu(1)–O(11B′)	165.7(5)	O(11A)–Cu(2)–O(10A′)	166.4(5)
O(11B)–Cu(1)–O(10C′)	88.7(5)	O(11A)–Cu(2)–O(11D′)	91.4(5)
O(10C)–Cu(1)–O(11B′)	88.6(5)	O(10D)–Cu(2)–O(10A′)	88.2(5)
O(10C)–Cu(1)–O(10C′)	164.9(5)	O(10D)–Cu(2)–O(11D′)	166.5(5)
O(11B)–Cu(1)–O(10C′)	89.4(5)	O(10A′)–Cu(2)–O(11D′)	89.3(6)
C(9B)–O(11B)–Cu(1)	115.6(6)	C(9A)–O(11A)–Cu(2)	119.0(7)
C(9B)–O(10B)–Cu(1′)	131.4(6)	C(9A)–O(10A)–Cu(2′)	126.5(7)
C(9C)–O(10C)–Cu(1)	121.9(6)	C(9D)–O(10D)–Cu(2)	127.8(7)
C(9C)–O(11C)–Cu(1′)	127.8(7)	C(9D)–O(11D)–Cu(2′)	118.1(7)
C(2p)–N(1p)–Cu(1)	131.0(7)		
C(6p)–N(1p)–Cu(1)	112.1(7)		

[CaCu(O$_2$CCH$_2$OC$_6$H$_4$Cl-2)$_4$(H$_2$O)$_5$] (**3**)

Cu–O(11B)	1.965(7)	Ca–O(10A)	2.458(7)
Cu–O(11A)	1.993(7)	Ca–O(10B)	2.419(8)
Cu–O(1w)	2.269(10)	Ca–O(2w)	2.470(8)
Cu–Ca	3.480(3)	Ca–O(3w)	2.407(10)
O(1w)–Cu–O(11A)	94.9(4)	O(10B)–Ca–O(10B′)	114.4(4)
O(1w)–Cu–O(11B)	90.9(4)	O(10B)–Ca–O(2w′)	145.8(4)
O(11A)–Cu–O(11B)	88.7(4)	O(10B)–Ca–O(3w′)	140.6(4)
O(11A)–Cu–O(11A′)	170.3(4)	O(2w)–Ca–O(3w)	78.4(4)
O(11A)–Cu–O(11B′)	91.2(4)	O(2w)–Ca–O(2w′)	132.9(5)
O(11B)–Cu–O(11B′)	178.2(4)	O(2w)–Ca–O(3w′)	72.6(5)
O(10A)–Ca–O(10B)	74.4(5)	O(3w)–Ca–O(3w′)	102.6(5)
O(10A)–Ca–O(2w)	72.9(5)	C(9A)–O(11A)–Cu	120.5(7)
O(10A)–Ca–O(3w)	78.4(5)	C(9A)–O(10A)–Ca	131.9(8)
O(10A)–Ca–O(10A′)	121.3(5)	C(9B)–O(11B)–Cu	116.3(7)
O(10A)–Ca–O(10B′)	74.7(5)	C(9B)–O(10B)–Ca	138.8(7)
O(10A)–Ca–O(2w′)	133.3(5)		
O(10A)–Ca–O(3w′)	144.5(5)		
O(10B)–Ca–O(2w)	66.8(5)		
O(10B)–Ca–O(3w)	84.5(5)		

Table 3. Comparative distances (Å) and angles (°) including torsion angles for the ligands in (**1**), (**2**), and (**3**) compared with those for (2-chlorophenoxy)ethanoic acid. For the latter, A and B are the two independent molecules in the asymmetric unit

	(**1**)		(**2**)			
	Ligand A	Ligand B	Ligand A	Ligand B	Ligand C	Ligand D
O(7) ··· O(10)	2.730(9)	2.680(9)	2.64(2)	2.69(2)	2.79(2)	2.64(2)
C(9)–O(10)	1.246(10)	1.225(9)	1.24(2)	1.24(1)	1.25(2)	1.23(2)
C(9)–O(11)	1.259(10)	1.279(8)	1.25(2)	1.26(1)	1.25(2)	1.26(1)
C(2)–C(1)–O(7)	116.3(7)	116.1(8)	118(1)	117(1)	120(1)	113(1)
C(6)–C(1)–O(7)	124.5(8)	124.8(7)	123(1)	124(1)	119(1)	124(1)
C(8)–C(9)–O(10)	119.6(7)	120.3(6)	116(1)	118(1)	119(1)	119(1)
C(8)–C(9)–O(11)	113.7(7)	115.1(6)	116(1)	115(1)	116(1)	113(1)
C(2)–C(1)–O(7)–C(8)	−117(1)	−159(1)	−150(1)	179(1)	+89(2)	+175(1)
C(1)–O(7)–C(8)–C(9)	−71(1)	+62(1)	+65(1)	−71(2)	+71(2)	+178(1)
O(7)–C(8)–C(9)–O(11)	+117(1)	−179(1)	−171(1)	+173(1)	−140(1)	+169(1)

	(**3**)		Acid	
	Ligand A	Ligand B	Molecule A	Molecule B
O(7) ··· O(10)	2.734(10)	2.685(10)	2.628(10)	2.651(10)
C(9)–O(10)	1.224(14)	1.259(14)	1.230(11)	1.213(11)
C(9)–O(11)	1.284(14)	1.260(15)	1.288(11)	1.305(11)
C(2)–C(1)–O(7)	115.7(10)	117.8(11)	115.0(8)	114.1(8)
C(6)–C(1)–O(7)	126.1(11)	121.4(11)	125.3(8)	125.0(8)
C(8)–C(9)–O(10)	118.4(10)	118.3(10)	123.6(8)	125.5(8)
C(8)–C(9)–O(11)	114.3(10)	115.0(10)	113.0(8)	110.1(8)
C(2)–C(1)–O(7)–C(8)	+174(1)	+164(1)	−179.4(8)	+179.9(8)
C(1)–O(7)–C(8)–C(9)	−50(1)	+178(1)	−175.1(8)	−173.2(8)
O(7)–C(8)–C(9)–O(11)	−158(1)*	−148(1)	−179.3(9)	−179.9(8)

* O(7)–C(8)–C(9)–O(10).

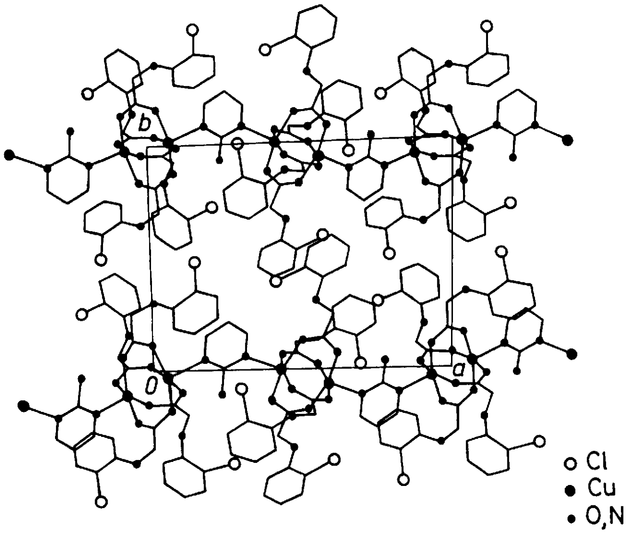

Figure 4. Perspective view of the packing of (**2**) in the unit cell down the *c* axis

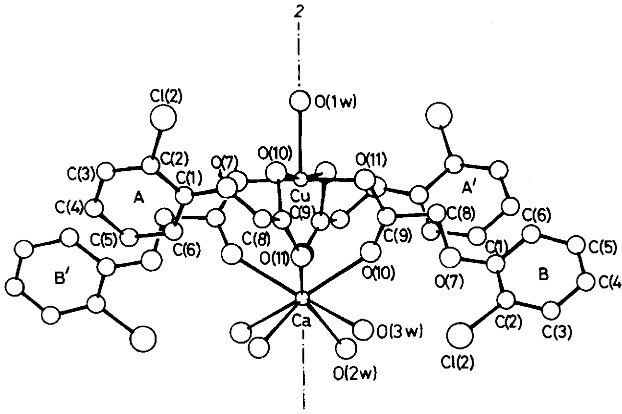

Figure 5. Molecular configuration and atom numbering scheme for $[CaCu(O_2CCH_2OC_6H_4Cl\text{-}2)_4(H_2O)_5]$ (**3**). Primed atoms are generated by a two-fold rotation operation

phenoxy)ethanoato-ligands in the three complexes are of considerable interest when compared with those of the uncomplexed acid.[10] This acid is unusual in itself in that it does not pack in a conventional manner in its unit cell about crystallographic centres of symmetry. Instead, it forms hydrogen-bonded cyclic dimers which occupy general positions with two independent molecules in the asymmetric unit of a triclinic cell. A prior structure determination of this acid[26] reported similar findings, but with a non-centrosymmetric unit cell (space group $P2_1$). An explanation, not confirmed by differential thermal–thermogravimetric analysis, was that a phase change in the crystal was occurring. It is possible that whatever the phenomenon, it may also be partially responsible for the anomalous solid-state behaviour of (**1**). Despite this, both independent acids are essentially planar, the preferred conformation of these phenoxyethanoic acid analogues having no C(2) and C(6) ring substitution.[27] The systematic features of the series of phenoxy acids, irrespective of the type of acid residue involved, *i.e.* ethanoic, 2-propanoic, or 2-methylpropanoic, are as follows. (*a*) The *exo*-C(1) bond angles are distorted, showing substantial expansion of the C(6)–C(1)–O(7) angle away from the steric interference of the C(8) methylene protons (Table 3). The only example where this is not the case is (2,6-dichlorophenoxy)ethanoic acid (122.9°),[27] presumably due to the equivalence of the 2- and 6-substituents. The distortion is also found for the anions of these acids when they are co-ordinated

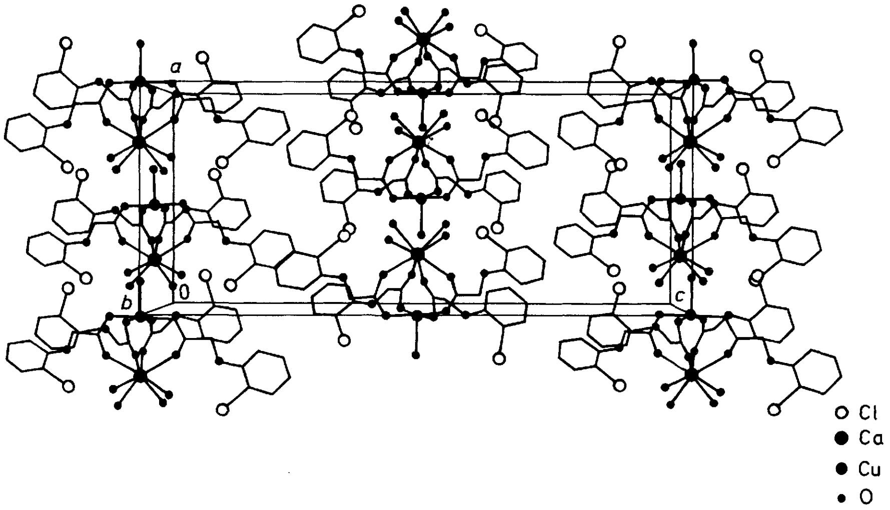

Figure 6. Perspective view of the packing of (**3**) in the unit cell showing the stacking of the dimers down the *a* axis at *c ca.* 0, $\frac{1}{2}$

to metal ions in complexes.[2–4] In the present examples, all ligands except ligand C of (**2**) retain this distortion, irrespective of the gross conformation of the oxo-ethanoate side-chain, *i.e.* whether it is anti-periplanar [torsion angle C(1)–O(7)–C(8)–C(9) *ca.* 180°] or synclinal (torsion angle *ca.* 90°). (*b*) The angles associated with the carboxylic acid group [C–C–O ('carbonyl') > 120°; C–C–O ('hydroxyl') < 120°] are significantly different and tend to retain their identity upon deprotonation, *i.e.* complexation. Coupled to this effect is the discrete difference between the C–OH [C(9)–O(11)] and C=O [C(9)–O(10)] bond distances (typically 1.30 and 1.20 Å respectively for the free acids), which tend to become more equidimensional upon complexation. However, it has been found that for this series at least, a distinctive difference also remains among the majority of the phenoxy ligands, including those for (**1**), (**2**), and (**3**). (*c*) The separation of the ether oxygen [O(7)] and the synplanar-related carboxyl oxygen is similar among the acid analogues, irrespective of the nature of the acid or the side-chain conformation [2.605—2.775 Å; 2.711 Å mean for 19 examples].[27] This interactive distance is also retained upon complexation [complexes (**1**) 2.730, 2.680 Å; (**2**) 2.639, 2.689, 2.788, 2.638 Å; and (**3**) 2.685, 2.734 Å] as has been the case in all previous examples. The values for the two crystallographically independent molecules of the free acid (2-chlorophenoxy)ethanoic acid are 2.628 and 2.651 Å.

General Discussion.—The atypical nature of the copper(II) complexes of 2-chloroethanoic acid when compared with the other monosubstituted phenoxyalkanoic acid analogues is, to say the least, puzzling. The anomaly continues into the nickel(II) complexes where μ-aqua-di-μ-[(2-chlorophenoxy)ethanoato-*O*,*O'*]bis{[(2-chlorophenoxy)ethanoato]bis(pyridine)nickel-(II)}-water (1/1)[1] provides an unprecedented example of a dimeric nickel species having two carboxyl bridges and a single water bridge. Introduction of other bulky groups into the 2-position of the phenoxy ring, *e.g.* a nitro-group[28] does not have an analogous effect on the stereochemistry of its metal complexes. *catena*-Diaquabis[(2-nitrophenoxy)ethanoato]-manganese(II) (octahedral), tetra-aquabis[(2-nitrophenoxy)-ethanoato]copper(II)-water (1/2) (tetragonally distorted octahedral), and bis(2-aminopyrimidine)aquabis[(2-nitrophenoxy)-ethanoato]copper(II) (square pyramidal) are relatively stereotypical. Although the nitro-group is somewhat larger than a chlorine in the 2-position, it is reasonable to assume that chlorine provides a more subtly interacting group which is uniquely favoured sterically and stabilizes the structures. This is possibly achieved *via* long-range interactions between the 2-chlorine and other groups in the structures.

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