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Metal–Phenoxyalkanoic Acid Interactions.
Part 3. Crystal and Molecular Structures of Tetra-μ-(2,4-dichlorophenoxyacetato)-bis[aquacopper(II)] dihydrate and Tetra-μ-(2,4,5-trichlorophenoxyacetato)bis-[pyridinecopper(II)]

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The crystal structures of tetra-μ-(2,4-dichlorophenoxyacetato)bis[aquacopper(II)] dihydrate (1) and tetra-μ-(2,4,5-trichlorophenoxyacetato)bis[pyridinecopper(II)] (2) have been determined by X-ray diffraction from diffractometer data and refined by least-squares to R 0.11 (2218 reflections) and 0.068 (2268 reflections) for (1) and (2) respectively. For (1), crystals are monoclinic, space group C2/c with Z = 4 in a cell of dimensions a = 36.98(3), b = 7.582(2), c = 14.972(5) Å, β = 105.52(5)° while for (2) the space group is P$\bar{1}$ with Z = 1 with a cell of dimensions a = 12.184(8), b = 13.719(7), c = 8.687(6) Å, α = 99.69(5), β = 99.15(5), γ = 114.01(4)°. Both compounds (1) and (2) consist of centrosymmetric tetra-carboxylate bridged dimer units of the copper acetate type, with Cu–Cu separations of 2.639(5) Å (1) and 2.716(7) Å (2). The copper and carboxylate oxygens lie approximately in the same plane in both (1) and (2) with a mean Cu–O distance of 1.972(10) Å and 1.973(12) Å respectively while the co-ordination sphere is completed in the axial positions by water oxygens [2.120(10) Å] in (1) and pyridine nitrogens [2.142(12) Å] in (2).

Introduction

Phenoxyalkanoic acid complexes of copper(II) are known to exist in a number of forms, differing not only in the number of molecules of water in the basic formula Cu(phenoxy)$_2$(H$_2$O)$_n$, n = 0–3, but also, in the diversity of complexing modes. These are reviewed in Part 1 of this series [1] and include monodentate [Cu(phenoxy)$_2$(H$_2$O)$_3$; Cu(*p*-methoxyphenoxy)$_2$(H$_2$O)$_2$·2H$_2$O], bidentate chelate [Cu(*p*-methoxyphenoxy)$_2$(H$_2$O)$_2$; Cu(*p*-nitrophenoxy)$_2$-(H$_2$O)$_2$; Cu(*p*-chlorophenoxy)$_2$(H$_2$O)$_2$] and a combination of bidentate chelate and bridging [Cu-(phenoxy)$_2$]. Although no structures of dimeric Cu$_2$(RCO$_2$)$_4$L$_2$ species of the copper acetate monohydrate type [2] have been reported to date the dark green crystalline bis(*o*-chlorophenoxyacetato)copper-(II) has a room temperature magnetic susceptibility of 1.50 BM, indicative of some degree of Cu–Cu interaction although the temperature dependence of the susceptibility is not consistent with a binuclear species [3]. It has been postulated [4] that in the aryl carboxylate series, steric effects are important in forcing the formation of dimer structures, *e.g.* Cu *o*-bromobenzoate [4] and Cu acetylsalicylate [5]. Substitution of halogen and alkyl groups about the benzene ring in the phenoxyalkanoic acids gives rise to herbicidally-active compounds which are commonly used commercially. The important members of this series are 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 4-chloro-2-methylphenoxyacetic acid (MCPA). The preparation and stability constants for copper complexes of 2,4-D and MCPA were reported as part of an early investigation of the feasibility of metal chelation as an *in vivo* mode of action theory for these compounds [6, 7] which was later refuted by Perrin [8]. In subsequent work on 2,4-D complexes of Cu(II) a number of forms have been isolated but none correspond to the Cu(2,4-D)$_2$(H$_2$O)$_5$ of ref. 7. A pale blue microcrystalline form was readily formed on treatment of aqueous ethanolic 2,4-D with excess CuCO$_3$ using the method previously described [1]. Loss of water at low temperature or on vacuum desiccation gave a pale green deliquescent form while in a non-aqueous solvent such as ethyl acetate, a turquoise crystalline solid (1) was obtained

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with a basic formula Cu(2,4-D)$_2$(H$_2$O)$_2$. Attempts to prepare a Cu(II)(2,4,5-T) complex by a similar method gave a product insoluble in all common solvents. However, digestion of this solid in ethanolic pyridine gave a turquoise crystalline adduct (2) with formula Cu(2,4,5-T)$_2$(py). The crystal structures of both (1) and (2) were determined to ascertain the possible existence of dimeric species and to compare the conformational aspects of the complexed ligands with those of the free acids, the crystal structures of which are known [9, 10]. Furthermore, a number of recent reviews of the structural systematics of dimeric carboxylate species [11–13] might now allow prediction of the occurrence of such compounds among the substituted phenoxyalkanoic acid complexes of Cu(II).

Experimental

Preparation

(a) $C_{32}H_{28}Cl_8Cu_2O_{16}$ (1) was prepared by the general method previously described [1]. Two distinct forms were obtained on crystallization from different solvents. From ethyl acetate, large diamond-shaped turquoise crystals of (1) corresponding to Cu(2,4-D)$_2$(H$_2$O)$_2$, were obtained. The pale blue non-crystalline form (1a) which first precipitated from aqueous ethanol was found by elemental analysis also to be a two-hydrate. Vacuum desiccation at ambient temperature or oven drying at low temperature of form (1a) resulted in conversion to a pale green static deliquescent powder (1b). Although the elemental analysis for this sample suggested a hemihydrate, it is believed that (1b) is an anhydrous compound since a steady weight increase was apparent during weighing. For (1): Found: C, 35.9; H, 2.74; Cl, 27.1%. Calc. for $C_{32}H_{28}Cl_8Cu_2O_{16}$; C, 35.6; H, 2.60; Cl 26.3. (Cu not determined). For (1a) Found: C, 35.8; H, 2.97; Cl, 27.3%. Calc. for $C_{16}H_{14}Cl_4CuO_8$; C, 35.6; H, 2.60; Cl, 26.3% (Cu not determined). For (1b); Found: C, 37.6; H, 2.29; Cl 26.8%. Calc. for $C_{16}H_{10}Cl_4CuO_6$, (H_2O), C, 38.1; H, 2.01; Cl, 28.2%: For $C_{16}H_{11}Cl_4CuO_{6.5}$, (½$H_2O$); C, 37.5; H, 2.16; Cl, 27.7% (Cu not determined.)

(b) $C_{42}H_{26}Cl_{12}Cu_2N_2O_{12}$ (2) was prepared by treating the pale green water/ethanol insoluble product formed by the reaction of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and copper(II) carbonate with pyridine in ethanol. Attempts to dissolve the initially-formed Cu-2,4,5-T reaction product in any of the common solvents were unsuccessful. Crystallization of (2) from aqueous ethanol produced green needles which were used for x-ray structure determination. For (2); Found: C 37.4; H 2.30; Cl 31.5%. Calc. for $C_{42}H_{26}Cl_{12}Cu_2N_2O_{12}$, C, 38.7; H, 2.01; Cl, 32.7% (Cu not determined). Although the analysis of (2) indicated a monohydrate, no evidence of a water of hydration was found in the structure determination stage.

X-ray Data

Data for both compounds were obtained from single crystals measuring 0.20 × 0.18 × 0.30 mm (1) and 0.05 × 0.12 × 0.20 mm (2), mounted about the *b* and *c* axes for (1) and (2) respectively. A Syntex P2$_1$ four-circle diffractometer was used. 2218(1) and 2268(2) reflections with $I > 2.5\sigma(I)$ were considered observed out of 3463(1) and 3985(2) unique reflections collected up to 2θ 50° using monochromatic Mo-Kα radiation. No corrections were made for absorption.

Crystal Data

Tetra-μ-(2,4-dichlorophenoxyacetato)bis[aquacopper(II)] dihydrate (I), $C_{32}H_{28}Cl_8Cu_2O_{16}$, M = 1078.6, Monoclinic, a = 36.98(3), b = 7.582(2), c = 14.972(5) Å, β = 105.52(5)°, U = 4045.3 Å^3, D_m = 1.75 (by flotation), Z = 4, D_c = 1.77, $F(000)$ = 2168, Space group $C2/c$ (C_{2h}^6, No. 15). Mo-Kα radiation, λ = 0.7107 Å, μ = 16.9 cm^{-1}.

Tetra-μ-(2,4,5-trichlorophenoxyacetato)bis[pyridinecopper(II)] (2), $C_{42}H_{26}Cl_{12}Cu_2N_2O_{12}$, M = 1302.7, Triclinic, a = 12.184(8), b = 13.719(7), c = 8.687(6) Å, α = 99.69(5), β = 99.15(5), γ = 114.01(4)°, U = 1265.1 Å^3, D_m = 1.70 (by flotation), Z = 1, D_c = 1.72, $F(000)$ = 650, Space group $P\bar{1}$ (C_i^1, No. 2), Mo-Kα radiation, μ = 15.7 cm^{-1}.

The structures of both compounds were solved by direct methods [14] and refined by full-matrix least-squares to final residuals $R[=\Sigma\|F_o - F_c\|/\Sigma|F_o|]$ of 0.110 and 0.068 and R_w $[=(\Sigma\omega\|F_o - F_c\|^2/\Sigma\omega|F_o|^2)^{1/2}]$ of 0.120 and 0.070 for (1) and (2) respectively. Because of the large number of parameters involved, not all of the heavy atoms were refined anisotropically. Furthermore, a $\sin\theta$ cutoff was used to reduce the number of reflections [2218 for (1) and 2268 for (2)] to lower the cost of refinement. However, most of the hydrogen positions were located in difference-Fourier syntheses and included in the refinement at fixed positions with the isotropic temperature factors (U) set invariant at 0.05 Å^2. A final difference-Fourier gave no features larger than 1.1 and 0.5 e Å^{-3} for (1) and (2) respectively. This large peak in (1) was adjacent to Cu and is interpreted as being due to the effects of extinction for which allowance could not be adequately made using the SHELX system. It is also responsible for the high residual R for (1). Partial correction for extinction was achieved by removal of 20(1) and 4(2) intense low-angle reflections before the final refinement cycle. Some disorder is in evidence in the pyridine ring in (2) where high thermal motion did not allow location of any hydrogen positions. In (1), considerable disorder is in evidence in the chlorine substituents of ring (B) where anisotropic thermal para-

TABLE I. Atomic co-ordinates ($\times 10^4$) for $[Cu_2(2,4\text{-}D)_4(H_2O)_2]2H_2O$ (1) and $[Cu_2(2,4,5\text{-}T)_4(py)_2]$ (2) with estimated standard deviations in parentheses.

(1)	x/a	y/b	z/c
Cu	2506(1)	6025(2)	−464(1)
O(H1)	1789(3)	2617(15)	−1432(9)
O(H2)	2519(2)	3732(12)	−1265(5)
H(OH11)	1533	3161	−1462
H(OH12)	1908	2473	−1634
H(OH21)	2343	3224	−1218
H(OH22)	2635	4190	−1564

	x/a	y/b	z/c	x/a	y/b	z/c
	Ligand (A)			Ligand (B)		
H(3)	328	5041	−4021	4255	14592	441
H(5)	255	10149	−3154	*		
H(6)	764	9870	−2425	3567	8966	−433
H(81)	1326	8687	−1201	2805	10437	−2160
H(82)	1499	9230	−1854	*		
C(1)	930(4)	7372(18)	−2624(9)	3501(4)	11709(18)	−682(9)
C(2)	746(4)	5856(19)	−3134(10)	3708(4)	13309(20)	−527(10)
C(3)	393(5)	6024(20)	−3712(10)	4044(5)	13422(22)	139(11)
C(4)	217(5)	7625(21)	−3775(10)	4196(5)	11896(24)	636(12)
C(5)	373(5)	9063(22)	−3301(11)	4005(5)	10333(23)	493(11)
C(6)	732(4)	8938(20)	−2728(10)	3669(5)	10246(22)	−160(11)
O(7)	1288(2)	7079(12)	−2095(5)	3172(2)	11723(12)	−1352(5)
C(8)	1455(4)	8567(20)	−1566(10)	3006(4)	10073(18)	−1708(9)
C(9)	1853(4)	8111(17)	−1005(9)	2803(4)	9202(18)	−1064(9)
O(10)	1992(2)	6887(12)	−1177(5)	2273(2)	4910(12)	440(5)
O(11)	2996(2)	5768(11)	432(5)	2728(2)	7583(12)	−1230(5)
Cl(2)	976(1)	3883(5)	−3017(3)	3513(1)	15147(5)	−1137(3)
Cl(4)	−238(1)	7802(7)	−4553(4)	4623(1)	12087(8)	1439(3)

(2)	x/a	y/b	z/c
Cu	8995(2)	185(2)	4567(2)
N(1p)	7429(8)	481(7)	3778(10)
C(2p)	6457(19)	−333(16)	2693(24)
C(3p)	5295(21)	−198(20)	2118(29)
C(4p)	5347(18)	873(17)	2803(23)
C(5p)	6426(21)	1683(17)	3640(26)
C(6p)	7504(17)	1470(15)	4108(21)

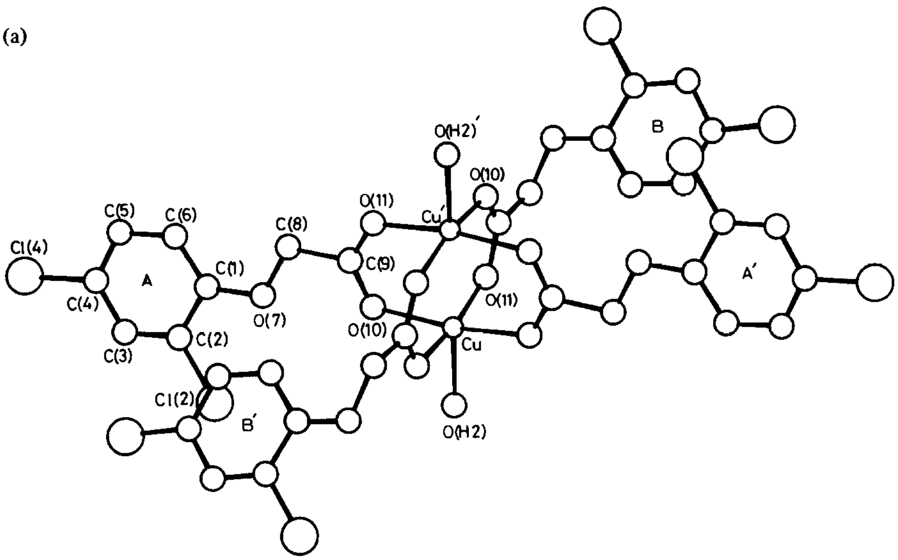
	x/a	y/b	z/c	x/a	y/b	z/c
	Ligand (A)			Ligand (B)		
C(1)	10500(9)	2479(8)	1261(12)	6542(8)	−4067(7)	−324(11)
C(2)	9501(10)	2631(9)	531(14)	5600(9)	−4119(8)	−1474(12)
C(3)	9427(11)	3615(9)	1086(14)	4909(10)	−5027(8)	−2791(12)
C(4)	10290(10)	4414(9)	2416(13)	5156(9)	−5931(8)	−2922(12)
C(5)	11220(10)	4219(8)	3187(12)	6117(9)	−5889(8)	−1792(11)
C(6)	11317(10)	3252(8)	2604(12)	6791(9)	−4984(7)	−487(11)
O(7)	10562(10)	1558(8)	537(11)	7167(9)	−3141(7)	881(12)
C(8)	11361(11)	1185(9)	1360(12)	8210(9)	−3040(7)	2005(11)
C(9)	10828(9)	735(7)	2793(12)	8874(9)	−1894(7)	3118(11)
O(10)	9837(10)	712(8)	2903(12)	11703(9)	1316(7)	6863(10)
O(11)	11528(10)	456(8)	3661(11)	10067(9)	1655(b)	6092(11)
Cl(2)	8397(5)	1642(4)	−1107(6)	5241(4)	−3005(3)	−1294(5)

(continued overleaf)

TABLE I. *(continued)*

	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
	Ligand (A)			Ligand (B)		
Cl(4)	10187(5)	5633(4)	3037(6)	4265(4)	−7066(3)	−4541(5)
Cl(5)	12315(4)	5198(3)	4893(6)	6482(4)	−6987(3)	−1968(6)
H(3)	8717	3832	650	4077	−4970	−3243
H(6)	12183	3392	3121	7418	−5012	366
H(81)	12154	1751	2062	8709	−3205	1585
H(82)	*			7926	−3549	2582

*Not located.



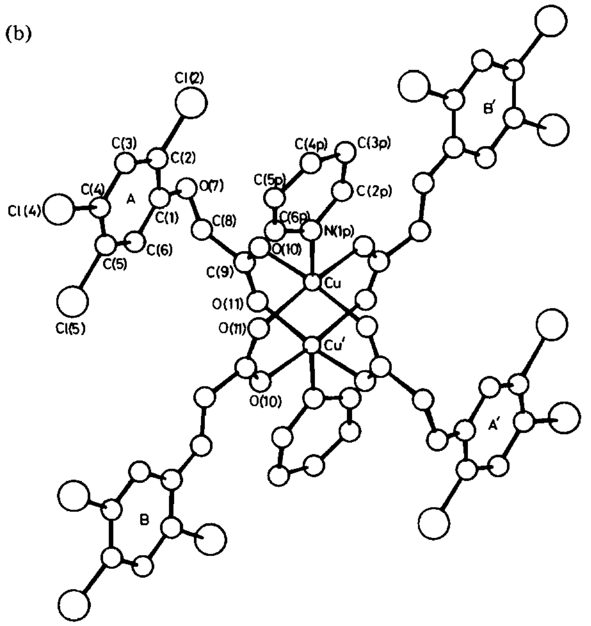


Fig. 1. Molecular configuration and atom naming scheme for (a), $[Cu_2(2,4\text{-}D)_4(H_2O)_2 2H_2O]$ (1) and (b), $[Cu_2(2,4,5\text{-}T)_4(py)_2]$ (2). A and B represent the two independent ligands in the centrosymmetric complex units, while A', B' Cu' and O(H2)' are the atoms or groups generated by the inversion operation.

TABLE IIa. Bond Distances (Å) and Angles (°) about the Co-ordination Spheres for (1) and (2) with Estimated Standard Deviations in Parentheses. "Atom'" indicates the second atom of the dimer unit generated by the symmetry operations ($\frac{1}{2} - x$, $\frac{1}{2} - y$, $-z$) (1) and ($-x$, $-y$, $-z$) (2).

Distances	(1)	(2)
Cu–Cu'	2.639(5)	2.716(7)
Cu–O(10A)	1.980(10)	1.971(10)
Cu–O(11A)'	1.955(10)	1.965(12)
Cu–O(10B)	1.978(10)	1.971(12)
Cu–O(11B)'	1.972(10)	1.984(12)
Cu–N(1p)	–	2.142(12)
Cu–O(H2)	2.120(10)	–
Angles		
O(10A)–Cu–O(11A)'	167.3(5)	166.1(10)
O(10A)–Cu–O(10B)'	86.9(5)	87.0(11)
O(10A)–Cu–O(11B)	91.4(5)	89.0(11)
O(10A)–Cu–N(1p)	–	95.7(12)
O(10A)–Cu–O(H2)	93.8(5)	–
O(10A)–Cu–Cu'	85.4(5)	81.7(9)
O(11A)'–Cu–O(10B)'	88.9(6)	89.5(10)
O(11A)'–Cu–O(11B)'	90.3(5)	91.3(10)
O(11A)'–Cu–N(1p)	–	98.1(11)
O(11A)'–Cu–O(H2)	98.6(5)	–
O(11A)'–Cu–Cu'	82.4(5)	84.4(9)
O(10B)'–Cu–O(11B)	168.3(6)	166.3(10)
O(10B)'–Cu–N(1p)	–	96.1(10)
O(10B)'–Cu–O(H2)	96.7(6)	–
O(11B)–Cu–O(H2)	122.1(6)	–
O(11B)–Cu–N(1p)	–	97.4(12)
O(10B)–Cu–Cu'	86.2(5)	83.0(10)
O(11B)–Cu–Cu'	82.3	83.4(11)
N(1p)–Cu–Cu'	–	177.3(10)
O(H2)–Cu–Cu'	177.0(5)	–

TABLE II(b). Intra-ligand Distances (Å) and Angles (°) for (1) and (2).

Distances	(1)		(2)	
	Ligand (A)	*Ligand (B)*	*Ligand (A)*	*Ligand (B)*
C(1)-C(2)	1.45(2)	1.42(2)	1.39(2)	1.37(2)
C(2)–C(3)	1.37(2)	1.37(2)	1.40(2)	1.39(2)
C(2)–Cl(2)	1.71(1)	1.72(1)	1.71(1)	1.74(1)
C(3)–C(4)	1.37(2)	1.41(2)	1.38(2)	1.38(2)
C(4)–Cl(4)	1.78(1)	1.72(1)	1.73(1)	1.73(1)
C(4)–C(5)	1.34(2)	1.37(2)	1.37(2)	1.38(2)
C(5)–C(6)	1.38(2)	1.36(2)	1.40(2)	1.38(2)
C(5)–Cl(5)	–	–	1.74(1)	1.73(1)
C(6)–C(1)	1.38(2)	1.40(2)	1.35(2)	1.40(2)
C(1)–O(7)	1.37(2)	1.35(2)	1.35(2)	1.34(2)
O(7)–C(8)	1.42(2)	1.43(2)	1.42(2)	1.42(2)
C(8)–C(9)	1.53(2)	1.52(3)	1.60(2)	1.51(2)
C(9)–O(10)	1.25(2)	1.24(2)	1.21(2)	1.25(2)
C(9)–O(11)	1.23(2)	1.27(2)	1.27(2)	1.24(2)
C(3)–H(3)	0.88	1.19	1.06	1.07
C(5)–H(5)	0.98	*	–	–
C(6)–H(6)	0.83	1.08	1.00	0.99
C(8)–H(81)	0.82	0.90	0.98	0.84
C(8)–H(82)	0.71	*	*	0.91

*Not located

(continued overleaf)

TABLE II(b). *(continued)*

Distances	(1)		(2)	
	Ligand (A)	*Ligand (B)*	*Ligand (A)*	*Ligand (B)*
N(1p)–C(2p)	–		1.32(3)	
C(2p)–C(3p)	–		1.52(3)	
C(3p)–C(4p)	–		1.46(3)	
C(4p)–C(5p)	–		1.31(3)	
C(5p)–C(6p)	–		1.47(3)	
C(6p)–N(1p)	–		1.30(3)	
O(H1)–H(OH11)	0.78		–	
O(H1)–H(OH12)	0.78		–	
O(H2)–H(OH21)	1.02		–	
O(H2)–H(OH22)	0.61		–	
Angles				
C(1)–C(2)–C(3)	119.7(13)	121.1(13)	120.0(18)	122.7(18)
C(1)–C(2)–Cl(2)	119.4(10)	118.4(10)	120.1(14)	119.1(14)
C(2)–C(3)–C(4)	118.9(13)	119.2(15)	120.9(18)	118.9(18)
C(3)–C(2)–Cl(2)	120.8(10)	120.4(11)	119.8(14)	118.2(14)
C(3)–C(4)–C(5)	123.7(14)	120.9(15)	118.2(16)	119.4(18)
C(3)–C(4)–Cl(4)	117.5(10)	117.6(10)	119.5(15)	118.3(15)
C(5)–C(4)–Cl(4)	118.8(10)	121.5(11)	122.2(14)	122.3(15)
C(4)–C(5)–C(6)	118.6(15)	119.3(15)	120.9(18)	121.0(18)
C(4)–C(5)–Cl(5)	–	–	119.7(14)	120.3(14)
C(6)–C(5)–Cl(5)	–	–	119.5(14)	118.6(14)
C(5)–C(6)–C(1)	121.5(4)	123.0(15)	121.4(18)	120.3(18)
C(6)–C(1)–C(2)	117.6(12)	116.5(12)	118.3(18)	117.9(18)
C(6)–C(1)–O(7)	127.4(12)	126.5(12)	126.0(16)	124.5(16)
C(2)–C(1)–O(7)	115.0(12)	116.9(12)	115.8(16)	117.6(16)
C(1)–O(7)–C(8)	113.8(12)	118.7(12)	120.4(15)	118.4(15)
O(7)–C(8)–C(9)	109.8(12)	112.2(12)	109.2(15)	110.0(15)
C(8)–C(9)–O(10)	118.1(11)	119.4(11)	116.9(16)	116.9(16)
C(8)–C(9)–O(11)	114.7(12)	114.5(12)	113.4(17)	114.3(17)
O(10)–C(9)–O(11)	127.2(12)	126.1(12)	129.7(16)	128.8(17)
C(9)–O(10)–Cu	119.7(10)	120.7(10)	122.7(13)	124.2(13)
C(9)–O(11)–Cu	125.0(11)	124.7(11)	121.9(14)	119.9(14)
N(1p)–C(2p)–C(3p)	–		120(3)	
C(2p)–C(3p)–C(4p)	–		116(3)	
C(3p)–C(4p)–C(5p)	–		118(3)	
C(4p)–C(5p)–C(6p)	–		121(3)	
C(5p)–C(6p)–N(1p)	–		122(3)	
C(6p)–N(1p)–C(2p)	–		120(3)	
C(6p)–N(1p)–Cu	–		122(3)	
C(2p)–N(1p)–Cu	–		117(3)	

meters (U_{11}, U_{22}, U_{33}, $\times 10^3$ Å^2) are 163, 96, 160 and 126, 209, 146 for Cl(2B) and Cl(4B) respectively.

Structure amplitudes and anisotropic thermal parameters are listed, deposited as supplementary material. Atomic co-ordinates are given in Table I while interatomic distances and angles are listed in Table II.

Discussion

Both complexes (1) and (2) form centrosymmetric dimeric units, the two copper centres bridged by four carboxylate groups of the substituted phenoxyacetic acid residues [2,4-D(1) and 2,4,5-T(2)] with Cu–O distances of 1.956, 1.973, 1.979, 1.979(10) Å and 1.970, 1.984, 1.971, 1.965(12) Å for (1) and (2) respectively (Figures 1a and 1b). The co-ordination sphere about each copper is completed in the axial positions in (1) by an oxygen from a water ligand at a distance of 2.120(10) Å and in (2) by a pyridine nitrogen at 2.142(12) Å. The bond distances and angles about the co-ordination spheres are listed in Table II(a) and are found to be comparable to those found for a number of similar dimeric copper species

TABLE III. Cu–Cu Separations (Å) for the Series of Known Dimeric Species of the Type $Cu_2(RCO_2)_4(L)_2$. (–) indicates an anhydrous form; (x) = X-ray; (n) = neutron; (m) = monoclinic form; (o) = orthorhombic form; (†) indicates e.s.d. not known.

R	L	Cu–Cu	Ref.
CH_2O–Ph(2,4-Cl_2)	H_2O	2.639(5)	This work
CH_2O–Ph(2,4,5-Cl_3)	py	2.716(7)	
H	urea	2.657(7)	a
H	NCS^-	2.716(2)	b
H	½ dioxane	2.58(1)	c
CH_3	H_2O	2.64(†) (x)	d
		2.616(1) (x)	e
		2.614(2) (n)	f
CH_3	py	2.645(3) (o)	g
		2.630(3) (m)	h
CH_3	NCS^-	2.643(3)	b
CH_3	quin	2.652(2)	i
CH_3	urea	2.624(†)	j
CH_3	pyz	2.583(1)	k
(CH_2)	H_2O	2.610(1)	l
CH_2F	urea	2.665(†)	m
CH_2F	quin	2.725(1)	n
CH_2Cl	urea	2.643(†)	o
CH_2Cl	quin	2.724(2)	i
CH_2Cl	2-Mepy	2.747(3)	p
CF_3	quin	2.886(2)	q
CCl_3	2-Clpy	2.766(3)	r
C_2H_5	(–)	2.578(4)	s
C_2H_5	py	2.631(2)	t
C_2H_5	3-Mepy	2.6312(4)	u
C_2H_5	½ dioxane	2.5634(4)	v
C_3H_7	(–)	2.565(†)	w
Ph	quin	2.671(2)	x
2-Br-Ph	H_2O	2.624(7)	y
2-acetyl-Ph	(–)	2.617(3)	z
CH_2–Ph	urea	2.626(†)	a′
C_8H_{15}	EtOH	2.644(†)	b′
$CH_2NHCOCH_3$	H_2O	2.666(1)	c′
CH_3	2-Mepy	2.671(4)	d′

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[13] The Cu–Cu separations for (1) and (2) are significantly different but fall within the range of 2.563 Å [tetra-μ-(propionato)bis[dioxanecopper(II)]] [18] to 2.886 Å [tetra-μ-(trifluoroacetato)bis[quinolinecopper(II)]] [19] found for the 31 dimeric structures given in Table III. The Cu–Cu range allowed by the tetracarboxylate cage is quite large and could be envisioned as being accommodated in a distortion of the O–C–O and O–Cu–Cu bond angles and a change of the C–O bond distance in the carboxyl group. Koh and Christoph [13] have correlated the M–M distance with the O–C–O angle, the C–O and M–O distances and the M–M–O angles for various dimeric species [M = Cu(II), Rh(II), Cr(II), Mo(II), Re(III) and results show that for M = Cu(II), the C–O distances are relatively constant, in contrast to the Cu–Cu–O angles which correlate well with Cu–Cu distance irrespective of the nature of R for the acid. Not surprisingly the O–C–O angles also increase with the Cu–Cu distance, the change being sensitive to the nature of R, a direct relationship existing with the value of pK_b for the corresponding conjugate base. This apparent inductive electronic effect, however, becomes of lesser importance in the acids being considered in (1) and (2) [2,4-D and 2,4,5-T] since the R group is considerably more extended.

For (1) and (2), a direct comparison is not tenable because of the different acids involved and because the axial co-ordinated water molecule in (1) has been replaced by pyridine in (2). This replacement by nitrogen bases has been shown to cause differences in the Cu–Cu distances in the dimeric monochloroacetic acid series in going from urea (2.643 Å) to quinoline (2.724 Å) to α-picoline (2.747 Å) [12].

TABLE IV Comparative Angular Features of the Phenoxyalkanoic Acid Residues in (1) and (2) and Those for the Un-co-ordinated Acids [9, 10] A and B are the two conformationally distinct acid ligands in the asymmetric unit Torsion angles are signed according to the convention of IUPAC [22] while the gross conformational motif is that used for α,β-saturated acids by Leiserowitz [23]

	C(8)–C(9)–O(10)	C(8)–C(9)–O(11)	C(2)–C(1)–O(7)–O(8)	C(1)–O(7)–C(8)–C(9)	O(7)–C(8)–C(9)–O(11)	Conformational motif
(1)A	118 1	114 7	+142 5	−32 6	+164 4	synclinal
B	119 4	114 5	−167 3	−78 6	+174 6	synclinal
(2)A	116 9	113 4	−165 4	+70 0	−175 4	synclinal
B	116 9	114 3	+174 1	−172 4	+165 7	antiperiplanar
2,4-D[a]	124 5	112 2	−179 1	−80 4	+173 1	synclinal
2,4,5-T[b]	124 4	112 7	+174 2	−171 6	−179 6	antiperiplanar

[a] 2,4-D = 2,4-dichlorophenoxyacetic acid [b] 2,4,5-T = 2,4,5-trichlorophenoxyacetic acid

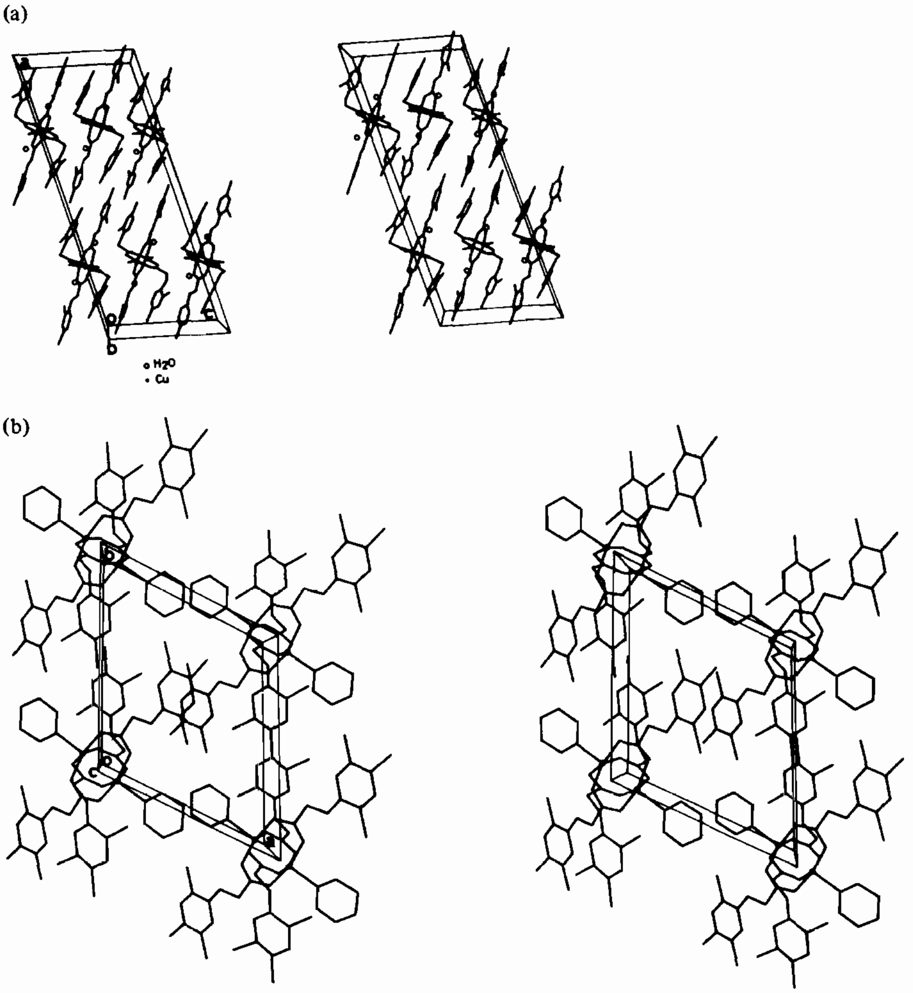

Fig 2 Stereoscopic views of the packing of (a) (1) and (b) (2) in the cell viewed perpendicular to the *ac* and *ab* planes respectively

Also paralleling the Cu–Cu separation is a progressive displacement of the Cu from the plane of the carboxylate oxygens in each copper coordination sphere, the distance between the least-squares planes through each oxygen set being constant (2 23 Å) The out-of-plane displacements for (1) and (2) are 0 24 and 0 23 Å respectively

Also of interest are the dimensional and conformational aspects of the substituted phenoxyacetate ligands in each complex. Intra-ligand distances and angles are listed in Table II(b) while torsion angles about the oxoacetic acid side-chains are in Table IV together with those for the uncomplexed acids 2,4-D [9] and 2,4,5-T [10]. Distance and angular parameters are very similar and do not warrant further comment. However in both (1) and (2), the two conformational motifs adopted are different. With (1), one of the 2,4-D ligands (B) is similar to the uncomplexed 2,4-D, adopting a similar synclinal conformation for the C(1)–O(7)–C(8)–C(9) torsion angle about the O(7)–C(8) vector. The second ligand (A), although still synclinal, has a considerably decreased angle (–32.6°). A similar difference in conformation is found for the two separate ligands in (2), one, (B) having the antiperiplanar conformation of the free acid while the second has a conformation similar to that found for 2,4-D [C(1)–O(7)–C(8)–C(9), +70.0°]. The change in conformation in each case is apparently due to the effects of packing in the unit cell, the planes of the substituted benzene rings adjusting to orient approximately parallel. (Figs. 2a, b). In the majority of complexes of phenoxyacetic acid, the preferred orientation of the ligand in the complexed form is the same as that found for the un-complexed acid, irrespective of the mode of complexation, *i.e.* unidentate, bidentate, bidentate-chelate, or bridging [1, 20]. Furthermore, on the basis of the relative distortions of the C–C–O angles about the carboxylate groups in both complexed ligands in (1) and (2), the retention of the synplanar–synplanar (*syn–syn*) conformational motif found for the free acids, is confirmed. This motif has also been found in phenoxyacetic acid [21] and in all known complexes of phenoxyacetic acid [1, 20]. Irrespective of the motif assumed, the intramolecular O(7) (ether)–O(10) (carbonyl) distance is similar [2.64, 2.73(2) Å for (1) and 2.63, 2.59(2) Å for (2)] and compares with 2.717(6) and 2.605(7) Å for 2,4-D and 2,4,5-T respectively. The mean value for 19 known examples of phenoxyalkanoic acids is 2.724 Å [21].

Hydrogen bonding associations appear to have no effect on the packing of (2) in the unit cell, with no intermolecular O–O contacts less than 3 Å. However, in (1), the water of hydration is linked in close intramolecular contacts with the co-ordinated water molecule (2.80 Å) and a carboxyl oxygen [O(11A)] (2.965 Å). The only other O–O contact less than 3 Å is 2.889 Å between the co-ordinated water and an ether oxygen (O7B).

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