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Metal–Phenoxyalkanoic Acid Interactions. Part 14.† The Crystal and Molecular Structures of Diaquabis(4-fluorophenoxyacetato)copper(II) Bis(4-fluorophenoxyacetic acid)Dihydrate and Tetra-μ-(4-fluorophenoxyacetato-0,0′)-bis[(2-aminopyrimidine)copper(II)]

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The crystal structures of two copper(II) complexes of 4-fluorophenoxyacetic acid (4-FPAH) have been determined by X-ray diffraction. [Cu(4-FPA)$_2$(H$_2$O)$_2$]·2(4-FPAH)·2H$_2$O (1) is triclinic, space group P1 *with* Z = 1 *in a cell of dimensions* a = 14.808(2), b = 9.832(2), c = 6.847(2) Å, α = 87.77(2), β = 98.41(2), γ = 112.33(2)° *and was refined to a residual of 0.038 for 1697 'observed' reflections. The coordination sphere in this complex is tetragonally distorted octahedral comprising two waters [Cu–O, 1.940(3) Å], two unidentate carboxylate oxygens [Cu–O, 1.942(2) Å] and two ether oxygens [Cu–O, 2.471(2) Å]. Two adducted [4-FPAH] acid molecules are linked to the un-coordinated oxygens of the acid ligands by hydrogen bonds [2.547(4) Å]. [Cu$_2$(4-FPA)$_4$(2-aminopyrimidine)$_2$] (2) is triclinic, space group* P1 *with* Z = 1 *in a cell of dimensions* a = 12.688(2), b = 11.422(2), c = 7.951(1) Å, α = 78.74(1), β = 107.51(1), γ = 75.78(1)°, *and was refined to a residual of 0.042 for 2683 'observed' reflections. (2) is a centrosymmetric tetracarboxylate bridged dimer with four similar Cu–O (equatorial) distances [1.967–1.987 Å; 1.977(3) Å mean] and the axial position occupied by the hetero nitrogen of the 2-aminopyrimidine ligand [Cu–N, 2.176(3) Å]. The Cu---Cu separation is 2.710(1) Å. Crystal data are also presented which confirm the isostructurality of complex (2) with [Cu$_2$(phenoxyacetate)$_4$(2-aminopyrimidine)$_2$], the Co^{II}, Mg^{II} and Mn^{II}4-fluorophenoxyacetate complexes with their phenoxyacetic and 4-chlorophenoxyacetic acid analogues, and of Cd^{II}4-fluorophenoxyacetate with Cd^{II} and Zn^{II} phenoxyacetates.*

†Part 13 [1].

Introduction

The reaction of phenoxyacetic acid (PAH) with copper(II) carbonate results in three chemical polymorphs with quite different complex stereochemistries. The first of these, [Cu(PA)$_2$]$_6$, is a cyclic hexamer with overall three-fold symmetry, and six-fold coordination about each copper centre [2]. The second, [Cu(PA)$_2$(H$_2$O)$_2$], is tetragonally distorted six-coordinate but is monomeric with both carboxyl and ether oxygens involved in a chelate mode [3]. On the other hand [Cu(PA)$_2$(H$_2$O)$_3$] has two unidentate PA ligands and three waters in square pyramidal coordination [4]. The second mode of complexation, has, apart from the tetra-carboxylate bridged dimer, the greatest incidence among the copper(II) analogues of phenoxyalkanoic acids. Isostructural complexes of the para-substituted acids are known, *e.g.* diaquabis(4-nitrophenoxyacetato)copper(II) [5], diaquabis(4-methoxyphenoxyacetato)copper(II) [5], and diaquabis(4-chlorophenoxyacetato)copper(II) [6]. Preliminary crystallographic work indicated that 4-fluorophenoxyacetic acid [4-FPAH] was similar, if not isomorphous with phenoxyacetic acid [7]. Consequently, it was assumed that some isostructurality was likely between the metal complexes of these acids. This was reinforced by the existence of an isomorphous and isostructural series of the type [Mn^{II}(phenoxy)$_2$(H$_2$O)$_2$]$_n$, where M^{II} = Co, Mg, Mn and phenoxy = phenoxyacetate, 4-chlorophenoxyacetate [8]. Isomorphism existed between the zinc(II) complexes of these same two acids [6] and has now extended to include the cadmium(II) analogue [9]. Because fluorine in these complexes precluded an elemental analysis, single crystal X-ray diffractometry provided an ideal method for analytically examining the series. Two

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copper complexes are reported. They are $[Cu(4\text{-}FPA)_2(H_2O)_2]\cdot 2[4\text{-}FPAH]\cdot 2H_2O$ (*1*) and its nitrogen base adduct $[Cu_2(4\text{-}FPA)_4(2\text{-aminopyrimidine})_2]$ (*2*), the first of which revealed the unexpected presence (for copper carboxylates) of uncomplexed acid molecules. Also reported are crystal data for Mg^{II}, Mn^{II}, Co^{II} and Cd^{II} 4-fluorophenoxyacetates and for the 2-aminopyrimidine adduct of copper(II) phenoxyacetate, which is analogous to complex (*2*).

Experimental

Preparation of Complexes

The divalent Cu, Mg, Mn, Co and Cd complexes of 4-fluorophenoxyacetic acid were prepared, as previously described [6], by reacting an aqueous ethanolic solution of the acid with the appropriate metal(II) carbonate. Compound (*2*) was formed from (*1*) by treating an aqueous solution of the complex with an ethanolic solution of 2-aminopyrimidine. Dark green crystals were readily obtained from the solution after partial evaporation at room temperature.

Collection of X-ray Data and Structure Solution

Details regarding cell parameters, data acquisition and structure solutions for (*1*) and (*2*) are given in Table I. Blocked-matrix least-squares refinement with anisotropic thermal parameters on all non-hydrogen atoms was used. Hydrogen atoms were located from difference-Fourier syntheses and included in the refinement at fixed positions with their isotropic U values set invariant at 0.05 Å^2. All computations were done using SHELXTL [10] [complex (*1*)] or SHELX-76 [11] [complex (*2*)]. Neutral atom scattering factors and values for the real and imaginary parts of the anomalous scattering factors were taken from ref. [12]. Final positional parameters are given in Table II while structure factors and anisotropic thermal parameters are available from the authors. Bond distances and angles are listed in Table III.

TABLE I. Cell data for $[Cu(4\text{-}FPA)_2(H_2O)_2]\cdot 2(4\text{-}FPAH)\cdot 2H_2O$, (*1*) and $[Cu_2(4\text{-}FPA)_4(2\text{-aminopyrimidine})_2]$, (*2*).

	(*1*)	(*2*)
Formula	$C_{32}H_{34}CuF_4O_{16}$	$C_{40}H_{34}Cu_2F_4N_6O_{12}$
M_r	814.1	993.8
a (Å)	14.808(2)	12.688(2)
b (Å)	9.832(2)	11.422(2)
c (Å)	6.847(2)	7.951(1)
α (°)	87.77(2)	78.74(1)
β (°)	98.41(2)	107.51(1)
γ (°)	112.33(2)	75.78(1)
V (Å^3)	912.0	1025.7
ρ_c (g cm^{-3})	1.482	1.608
ρ_f (g cm^{-3})	1.50	1.61
Z	1	1
μ (cm^{-1})	7.21	11.70
$F(000)$	419	506
Space Group	$P\bar{1}$	$P\bar{1}$
Data Collection		
a. diffractometer	Nicolet R3m	Nicolet R3m
b. radiation	Mo Kα	Mo Kα
c. $2\theta_{max}$ (°)	44	44
d. unique reflections measured	1906	3503
e. crystal size (mm)	0.50 × 0.30 × 0.14	0.42 × 0.25 × 0.12
Structure Solution	Direct methods	Direct methods
Refined	Blocked matrix	Blocked matrix
a. method used	Least squares	Least squares
b. R	0.038	0.042
c. R_w	0.042	0.044
d. w* A	1.0	2.1
B	4.9×10^{-4}	6.4×10^{-4}
e. data used	1697	2683
f. discrimination	$I > 2.5\ \sigma(I)$	$I > 2.5\ \sigma(I)$

* $w = A/(\sigma^2 F_0 + BF_0^2)$.

TABLE II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Cu(4\text{-FPA})_2(H_2O)_2]\cdot 2(4\text{-FPAH})\cdot 2(H_2O)$, (*1*) and $[Cu_2(4\text{-FPA})_4(2\text{-aminopyrimidine})_2]$, (*2*). $U_{eq*}/[(U_{11}\cdot U_{22}\cdot U_{33})^{1/3}]$.

Atom	*x/a*	*y/b*	*z/c*	$U_{eq*/iso}$	Atom	*x/a*	*y/b*	*z/c*	$U_{eq*/iso}$
a. $[Cu(4\text{-FPA})_2(H_2O)_2]\cdot 2(4\text{-FPAH})\cdot 2(H_2O)$ (*1*)									
Cu	0	0	0	35(1)*	Hw(11)	213	−1598	1287	50
Ow(1)	−768(2)	1048(3)	−1397(4)	49(1)*	Hw(12)	1196	−421	1472	50
Ow(2)	−1043(2)	3110(3)	552(4)	58(1)*	Hw(21)	−583	3420	369	50
					Hw(22)	−1411	2800	777	50
(4-FPA) ligand					(4-FPAH) molecule				
C(1)	−2254(3)	−2709(4)	1211(5)	41(2)*		3057(3)	−1138(4)	4185(6)	51(2)*
C(2)	−2177(3)	−3589(4)	−211(6)	56(2)*		3205(4)	−122(5)	2701(7)	71(2)*
C(3)	−2898(4)	−4962(5)	−622(7)	67(2)*		3893(4)	1300(5)	3078(8)	80(2)*
C(4)	−3685(4)	−5416(4)	400(7)	62(2)*		4421(4)	1652(5)	4893(7)	71(2)*
F(4)	−4384(2)	−6797(3)	24(5)	99(2)*		5101(3)	3043(3)	5228(5)	113(2)*
C(5)	−3784(3)	−4565(5)	1774(7)	62(2)*		4298(4)	686(5)	6360(8)	67(2)*
C(6)	−3061(3)	−3188(4)	2204(6)	56(2)*		3600(3)	−746(4)	6026(6)	57(2)*
O(7)	−1470(2)	−1371(3)	1600(4)	48(1)*		2349(2)	−2512(3)	3676(4)	55(1)*
C(8)	−1488(3)	−473(4)	3136(5)	44(2)*		2101(3)	−3538(4)	5199(6)	50(2)*
C(9)	−543(3)	865(4)	3453(5)	37(2)*		1247(3)	−4876(4)	4386(5)	44(2)*
O(10)	121(2)	1084(2)	2400(3)	38(1)*		843(2)	−5031(3)	2705(4)	57(1)*
O(11)	−484(2)	1712(3)	4831(3)	46(1)*		969(3)	−5875(3)	5733(4)	68(1)*
H(2)	−1618	−3246	−915	50		3497	−1448	7069	50
H(3)	−2852	−5591	−1610	50		4690	979	7631	50
H(5)	−4351	−4907	2453	50		4001	2017	2055	50
H(6)	−3117	−2562	3182	50		2832	−400	1410	50
H(81)	−1573	−1024	4330	50		2654	−3801	5680	50
H(82)	−2028	−156	2786	50		1930	−3115	6259	50
H(11)	–	–	–	–		1415	−6022	5512	50
b. $[Cu_2(4\text{-FPA})_4(2\text{-aminopyrimidine})_2]$ (*2*)									
Cu	1030.4(4)	4458.3(4)	4872.9(7)	26.6(3)*	H(4)p	5652	1978	4828	50
N(1)p	2750(3)	3596(3)	4883(4)	30(2)*	H(5)p	4365	673	5425	50
C(2)p	3591(3)	4155(4)	4845(6)	34(2)*	H(6)p	2410	1992	5267	50
N(21)p	3363(3)	5363(3)	4738(6)	43(2)*	H(21)p	3741	5866	4457	50
N(3)p	4659(3)	3552(3)	4916(5)	37(2)*	H(22)p	2690	5959	4167	50
C(4)p	4900(4)	2333(4)	5059(7)	44(3)*					
C(5)p	4114(4)	1688(5)	5147(8)	48(3)*					
C(6)p	3045(4)	2369(4)	5052(7)	45(3)*					
Ligand A					Ligand B				
C(1)	3152(4)	6210(4)	9725(6)	42(3)*		1467(4)	9415(4)	2029(6)	36(2)*
C(2)	4317(5)	6132(5)	10639(8)	56(3)*		2418(4)	9243(4)	1490(6)	41(2)*
C(3)	4736(6)	7084(7)	10027(10)	78(4)*		2812(4)	10240(5)	978(7)	48(3)*
C(4)	4012(7)	8074(7)	8590(10)	86(5)*		2228(4)	11401(4)	1011(7)	49(3)*
F(4)	4401(5)	9044(5)	7984(7)	142(4)*		2619(3)	12376(3)	523(5)	75(2)*
C(5)	2885(7)	8174(6)	7649(8)	71(4)*		1290(4)	11595(4)	1536(8)	47(3)*
C(6)	2433(5)	7231(5)	8241(7)	54(3)*		889(4)	10610(4)	2030(7)	43(3)*
O(7)	2837(3)	5213(3)	10421(4)	43(2)*		1179(3)	8345(3)	2545(5)	44(2)*
C(8)	1631(4)	5383(5)	9968(7)	44(3)*		188(4)	8463(4)	3038(6)	36(2)*

(Continued overleaf)

TABLE II. *(Continued)*

Atom	x/a	y/b	z/c	$U_{eq*/iso}$	Atom	x/a	y/b	z/c	$U_{eq*/iso}$
C(9)	1021(4)	5240(4)	8106(6)	32(2)*		71(3)	7166(3)	3639(5)	29(2)*
O(10)	1622(2)	4754(3)	7288(4)	38(2)*		858(2)	6231(2)	3753(4)	35(2)*
O(11)	−69(2)	5626(3)	7540(4)	42(2)*		−808(2)	7143(2)	4030(4)	42(2)*
H(2)	4828	7314	11971	50		2819	8337	1439	50
H(3)	5556	8904	10846	50		3433	10244	188	50
H(5)	2430	7082	6383	50		822	12430	1475	50
H(6)	1642	5235	7774	50		209	10762	2424	50
H(81)	1154	6298	9858	50		352	8808	4222	50
H(82)	1554	4792	10863	50		−555	9085	1974	50

TABLE III. Bond Distances (Å) and Angles (Degrees) for (*1*) and (*2*). Primed Atoms are generated by the Inversion Operation (−x, −y, −z).

a. Coordination Sphere

(i) Distances

(*1*)		(*2*)			
Cu–Ow(1)	1.940(3)	Cu–N(1)p	2.176(3)	Cu–O(11)A′	1.974(3)
Cu–O(10)A	1.942(2)	Cu–O(10)A	1.967(3)	Cu–O(11)B′	1.987(3)
Cu–O(7)A	2.471(2)	Cu–O(10)B′	1.979(3)	Cu–Cu′	2.710(1)

(ii) angles

(*1*)		(*2*)			
Ow(1)–Cu–O(7)A	86.6(1)	N(1)p–Cu–O(10)A	94.2(1)	O(10)B–Cu–O(11)A′	89.6(1)
Ow(1)–Cu–O(10)A	89.4(1)	N(1)p–Cu–O(10)B	98.8(1)	O(10)B–Cu–O(11)B′	165.9(2)
O(7)A–Cu–O(10)A	73.0(1)	N(1)p–Cu–O(11)A′	99.7(1)	O(11)A′–Cu–O(11)B′	87.2(1)
Cu–O(7)A–C(8)A	107.7(2)	N(1)p–Cu–O(11)B′	95.3(1)	Cu–O(10)A–C(9)A	126.1(3)
Cu–O(7)A–C(1)A	72.0(2)	O(10)A–Cu–O(10)B	87.5(1)	Cu–O(10)B–C(9)B	121.7(2)
Cu–O(10)A–C(9)A	125.9(2)	O(10)A–Cu–O(11)A′	166.1(1)	Cu–O(11)A′–C(9)A′	121.5(2)
		O(10)A–Cu–O(11)B′	92.2(1)	Cu–O(11)B′–C(9)B′	122.6(2)
		Cu–N(1)p–C(2)p	127.3(3)	Cu–N(1)p–C(6)p	116.5(3)

b. Intraligand

(i) distances

(*2*)
2-aminopyrimidine ligand

N(1)p–C(2)p	1.367(6)	N(3)p–C(4)p	1.329(6)
N(1)p–C(6)p	1.334(6)	C(4)p–C(5)p	1.378(8)
C(2)p–N(3)p	1.351(5)	C(5)p–C(6)p	1.372(7)
C(2)p–N(21)p	1.323(6)		

	(*1*)		(*2*)	
	(4-FPA) ligand	(4-FPAH) molecule	Ligand A	Ligand B
C(1)–C(2)	1.372(6)	1.378(6)	1.410(7)	1.384(7)
C(1)–C(6)	1.377(6)	1.375(6)	1.383(6)	1.394(6)
C(1)–O(7)	1.388(4)	1.387(4)	1.363(7)	1.376(6)

(Continued on facing page)

TABLE III. *(Continued)*

C(2)–C(3)	1.374(6)	1.389(6)	1.384(11)	1.384(8)
C(3)–C(4)	1.366(7)	1.349(7)	1.347(8)	1.373(7)
C(4)–C(5)	1.342(7)	1.339(7)	1.367(11)	1.361(9)
C(4)–F(4)	1.365(4)	1.359(5)	1.374(11)	1.356(7)
C(5)–C(6)	1.380(4)	1.398(5)	1.399(11)	1.375(8)
O(7)–C(8)	1.409(5)	1.410(5)	1.419(6)	1.412(6)
C(8)–C(9)	1.507(5)	1.492(5)	1.510(7)	1.521(6)
C(9)–O(10)	1.252(2)	1.204(4)	1.248(6)	1.251(6)
C(9)–O(11)	1.254(4)	1.311(4)	1.257(6)	1.248(6)

(ii) angles

	(*2*) 2-aminopyrimidine ligand		
C(2)p–N(1)p–C(6)p	116.1(4)	C(2)p–N(3)p–C(4)p	117.1(4)
N(1)p–C(2)p–N(3)p	124.2(4)	N(3)p–C(4)p–C(5)p	122.6(4)
N(1)p–C(2)p–N(21)p	118.9(4)	C(4)p–C(5)p–C(6)p	116.8(5)
N(3)p–C(2)p–N(21)p	116.9(4)	C(5)p–C(6)p–N(1)p	123.2(5)

	(*1*) (4-FPA) ligand	(4-FPAH) molecule	(*2*) Ligand A	Ligand B
C(6)–C(1)–C(2)	120.2(3)	119.9(3)	120.5(5)	119.6(5)
C(6)–C(1)–O(7)	123.7(4)	124.5(4)	125.2(5)	125.3(5)
C(2)–C(1)–O(7)	116.1(4)	115.6(3)	114.4(4)	115.1(4)
C(1)–C(2)–C(3)	119.9(4)	119.9(4)	119.3(4)	120.7(4)
C(2)–C(3)–C(4)	118.7(5)	119.0(5)	119.0(7)	118.1(5)
C(3)–C(4)–C(5)	122.4(4)	122.5(4)	123.4(8)	122.4(5)
C(3)–C(4)–F(4)	118.3(4)	118.2(4)	120.1(7)	118.1(5)
C(5)–C(4)–F(4)	119.2(4)	119.3(4)	116.5(5)	119.5(4)
C(4)–C(5)–C(6)	119.3(4)	119.6(4)	118.9(5)	119.8(5)
C(5)–C(6)–C(1)	119.5(4)	119.1(4)	118.9(5)	119.4(5)
C(1)–O(7)–C(8)	118.1(3)	117.4(3)	117.2(3)	118.0(3)
O(7)–C(8)–C(9)	110.5(3)	108.7(3)	114.8(5)	108.8(3)
C(8)–C(9)–O(10)	121.2(3)	124.8(3)	118.6(4)	118.5(3)
C(8)–C(9)–O(11)	114.9(4)	112.0(3)	115.1(4)	115.3(3)
O(10)–C(9)–O(11)	123.9(3)	123.1(3)	126.3(4)	126.2(3)

Single crystal diffractometry using an Enraf–Nonius Weissenberg goniometer confirmed that the 4-fluorophenoxyacetic acid complexes of Co^{II}, Mg^{II} and Mn^{II} with formula $[M(phenoxy)_2(H_2O)_2]_n$ were isomorphous with corresponding isomorphous sets of phenoxyacetic and 4-chlorophenoxyacetic acid complexes [8] respectively. In addition, the 4-fluorophenoxyacetic acid complex of Cd^{II}, with general formula $[M(phenoxy)_2(H_2O)_2]$, was found to be isomorphous with the Cd^{II} [9], and Zn^{II} [6] phenoxyacetate complexes. However, the crystalline product in the case of the Zn^{II}/4-FPAH reaction was different from that reported for the isomorphous Zn^{II} and Cd^{II} compounds (very thin pseudo-hexagonal plates, unsuitable for X-ray analysis, *cf.* large prismatic needles). Measured density (1.72 g cm^{-3}) was also greater than found in $[Zn(PA)(H_2O)_2]$ (1.64 g cm^{-3}) or $[Zn(4\text{-}CPA)_2(H_2O)_2]$ (1.71 g cm^{-3}) [6]. The product from the crystallization of cadmium 4-chlorophenoxyacetate was similarly platy and was proved (elemental analysis) to have the basic stoichiometry $[Cd(4\text{-}CPA)_2(H_2O)_2]$.

The 2-aminopyrimidine adduct of copper(II) phenoxyacetate was also found to be isomorphous with complex (*2*).

Crystal data for these compounds are as follows:

A.* $[Co(4\text{-}FPA)_2(H_2O)_2]_n$, $C_{16}H_{16}F_2CoO_8$, M_r = 433.2, a = 6.9(1), b = 7.5(1), c = 34.9(3) Å, V = 1806 Å^3, ρ_c = 1.59 g cm^{-3}, ρ_m = 1.61 g cm^{-3} (Z = 4), $F(000)$ = 884, space group *Pbca*.

B.* $[Mg(4\text{-}FPA)_2(H_2O)_2]_n$, $C_{16}H_{16}F_2MgO_8$, M_r = 398.6, a = 7.0(1), b = 7.5(1), c = 34.9(3) Å, V = 1832 Å^3, ρ_c = 1.44 g cm^{-3}, ρ_m = 1.46 g cm^{-3} (Z = 4), $F(000)$ = 824, space group *Pbca*.

*Accurate cell for the isomorphous $[Mn(PA)_2(H_2O)_2]_n$ is a = 7.007(4), b = 7.699(4), c = 33.22(2) Å [8].

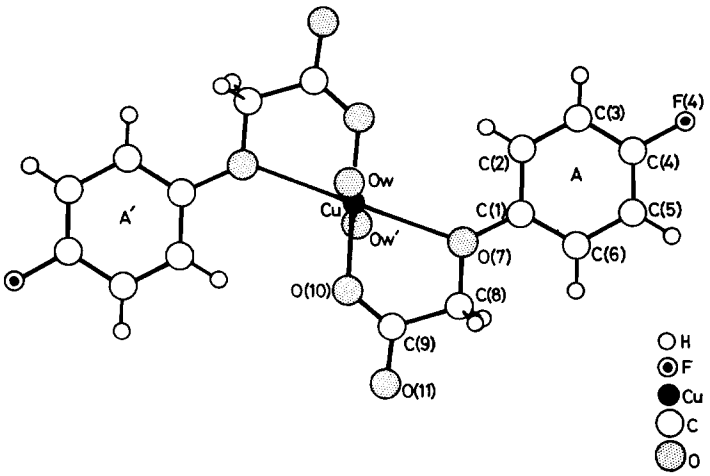

Fig. 1. The complex unit in the compound $[Cu(4\text{-}FPA)_2(H_2O)_2]\cdot 2(4\text{-}FPAH)\cdot 2(H_2O)$, (*1*).

C.* $[Mn(4\text{-}FPA)_2(H_2O)_2]_n$, $C_{16}H_{16}F_2MnO_8$, M_r = 429.2, a = 7.1(1), b = 7.6(1), c = 34.7(1) Å, V = 1872 Å^3, ρ_c = 1.52 g cm^{-3}, ρ_m = 1.55 g cm^{-3} (Z = 4), $F(000)$ = 876, space group *Pbca*.

D.† $[Cd(4\text{-}FPA)_2(H_2O)_2]$, $C_{16}H_{16}CdF_2O_8$, M_r = 486.7, a = 11.9(1), b = 5.45(5), c = 13.7(1), β = 99.0(5)°, V = 878 Å^3, ρ_c = 1.84 g cm^{-3}, ρ_m = 1.85 g cm^{-3} (Z = 2), $F(000)$ = 484, space group $C2$.

E. $[Cd(4\text{-}CPA)_2(H_2O)_2]$ (4-CPA = 4-chlorophenoxyacetate) [elemental analysis only]. Found: C, 37.0; H, 3.12; Cl, 13.3%. Calculated for $C_{16}H_{16}CdCl_2O_8$: C, 37.0; H, 3.10; Cl, 13.6%.

F.‡ $[Cu_2(PA)_2(2\text{-aminopyrimidine})_2]$ (PA = phenoxyacetate), $C_{40}H_{38}Cu_2N_6O_{12}$, M_r = 921.9, a = 12.6(1), b = 11.4(1), c = 8.0(1) Å, α = 79(1), β = 108(1), γ = 77(1)°, V = 1022 Å^3, ρ_c = 1.50 g cm^{-3}, ρ_m = 1.52 (Z = 1), $F(000)$ = 474, space group $P\bar{1}$. Elemental analysis. Found: C, 51.9; H, 4.23; N, 9.11%. Calculated for $C_{40}H_{38}Cu_2N_6O_{12}$: C, 52.1; H, 4.15; N, 9.11%.

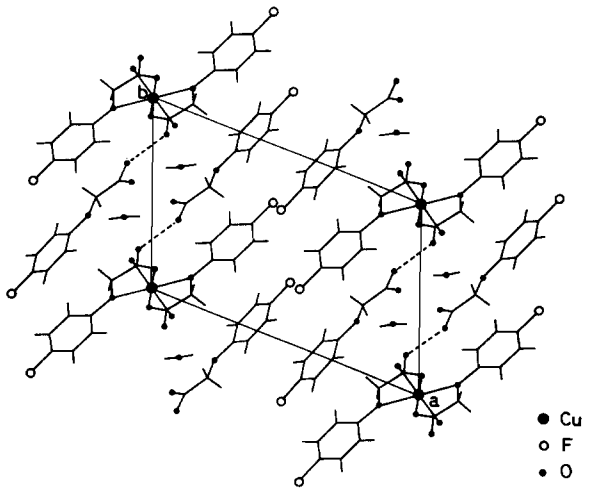

Fig. 2. The packing of (*1*) in the cell viewed perpendicular to *ab*.

Discussion

a. [Cu(4-FPA)$_2$(H$_2$O)$_2$]·2(4-FPAH)·2H$_2$O (1)

The structure of (*1*) consists of centrosymmetric six-coordinate CuO_6 complex units (Fig. 1) which are bound by short hydrogen bonds [O(11)A---O(11)B, 2.547(4) Å] to free acid molecules (Fig. 2). The complex copper(II) stereochemistry is tetragonally distorted octahedral [Cu–O, 1.940(3), 1.942(3) Å and 2.471(2) Å] with the bonds elongated to the ether oxygens of the phenoxy acid and completing five-membered chelate rings. The oxygens of the square plane consist of two from the carboxylate groups and two from water ligands. In this respect, the structure is similar to diaquabis(phenoxyacetato)-copper(II) [Cu–O, 1.94, 1.98, 2.48 Å] [3], diaquabis(4-methoxyphenoxyacetato)copper(II) [Cu–O, 1.945(3), 1.955(2), 2.432(3) Å] [2] and diaquabis-(4-chlorophenoxyacetato)copper(II) [Cu–O, 1.956-(4), 1.960(4), 2.406(4) Å] [6]. However, the presence of the free acid molecules has no precedent among the copper(II) phenoxy series nor does it have incidence among examples of copper(II) carboxylates. This phenomenon is reasonable, particularly among

*Accurate cell for the isomorphous $[Mn(PA)_2(H_2O)_2]_n$ is a = 7.007(4), b = 7.699(4), c = 33.22(2) Å [8].

†Accurate cell for $[Zn(PA)_2(H_2O)_2]$ [6] is a = 11.625(3), b = 5.221(1), c = 13.767(4) Å, β = 101.05(5)°; and for $[Cd(PA)_2(H_2O)_2]$ [9] is a = 11.801(2), b = 5.484(1), c = 13.431(3) Å, β = 100.87(2)°.

‡Accurate cell for $[Cu(4\text{-}FPA)_2(2\text{-aminopyrimidine})_2]$, see (*2*), Table I.

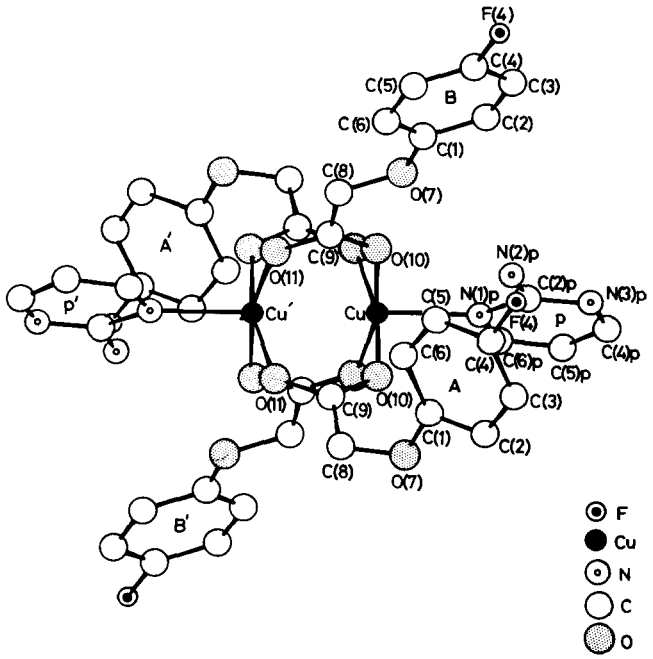

Fig. 3. Atom naming scheme for $[Cu_2(4\text{-FPA})_4(2\text{-aminopyrimidine})_2]$, (*2*).

the complexes of the phenoxy acids, where the planarity of the ring system tends to result in regular molecular stacking effects in the solid state. Furthermore, in the usual method employed for the preparation of these complexes from metal carbonate, unreacted acid is often present in the crystallizing solution. This has been shown in some systems to exert a significant influence on the nature of the final product obtained. Manganese(II) provides the most graphic of the examples, giving, with 2,4,5-trichlorophenoxyacetic acid (2,4,5-TH), three distinctly different chemical polymorphs depending on the relative concentrations of acid and metal ion. The final product of the crystallization, with 2,4,5-TH in excess, is $[Mn(2,4,5\text{-T})_2(H_2O)_4]\cdot 2(2,4,5\text{-TH})$, while a second form is $[Mn(2,4,5\text{-T})\cdot(H_2O)_5]^+(2,4,5\text{-T})^-$ [13]. In the case of the Mn-2,4,5-T adduct, the carboxyl groups of the free acid and those of the complexed ligand are also linked by short hydrogen bonds (2.46 Å). Also, the adduct, $[K(PTA)(PTAH)]_n$ [PTAH = (phenylthio)acetic acid], has an analogous bonding system with carboxyl linked hydrogen bonds (2.494 Å) [14].

Intermolecular hydrogen bonding interactions involving the lattice water molecules stabilize the structure [O(10)B---Ow(2), 2.840 Å; Ow(1)---Ow(2), 2.656 Å], in addition to those between the bonded water [Ow(1)] and the free acid [O(10)B] (2.905 Å) (Fig. 2). The structures of the other copper(II) monomers of this series are generally devoid of such intermolecular hydrogen bonding interactions.

b. [Cu_2(4-FPA)$_4$(2-aminopyrimidine)$_2$] (2)

Complex (*2*) forms discrete centrosymmetric tetracarboxylate bridged dimers of the copper(II) acetate hydrate type [15] (Fig. 3). The bond distances and angles about the dimer are quite normal for this system with Cu–O (equatorial) distances ranging from 1.967–1.987 Å [1.977(3) Å mean] compared with a series mean of 1.96 Å [16]. The Cu---Cu separation is 2.710(1) Å. The axial donor group is a hetero nitrogen of the 2-aminopyrimidine ligand [Cu–N, 2.176(3) Å]. This is the first example among the copper(II) complexes in which 2-aminopyrimidine acts to give discrete monomers. The only other dimer system, $[Cu_2(2\text{-chlorophenoxy})_4(2\text{-aminopyrimidine})]_n$, is extended into a polymer system *via* both hetero nitrogens of the pyrimidine ring [1]. The comparative Cu---Cu and Cu–N (axial) distances are 2.700, 2.730 Å and 2.244, 2.248 Å respectively for the two crystallographically independent dimers. The longer Cu–N distance is consistent with an increased Cu–L distance associated with dimer-polymer structures rather than with discrete dimers. Another copper(II) complex of 2-aminopyrimidine is bis(2-aminopyrimidine)-bis(4-amino-3,5,6-trichloropyridine-2-carboxylato)copper-(II) [15], which is a monomeric orthorhombically distorted six-coordinate copper(II) species with *trans*-related pyrimidines [Cu–N, 2.048(6), 2.054(6) Å]. The complex from which the latter adduct is formed, aquabis(4-amino-3,5,6-trichloropyridine-2-carboxylato)copper(II) [17], has in contrast, five-coordinate square pyramidal stereochemistry for

copper. Aquabis(2-aminopyrimidine)bis(2-nitrophenoxyacetato)copper(II) is also square pyramidal [18].

The 2-aminopyrimidine ligands in (*2*) are structurally similar to those for the other complexes and for the free ligand [19]. The 2-amino group stabilizes the dimer formation through hydrogen bonds with adjacent carboxyl oxygens [O(10)B, 2.907 Å] while the dimers themselves are characteristically non-associated (Fig. 4). The ready formation of (*2*) from (*1*) under mild conditions by addition of 2-aminopyrimidine may be considered the result of dissociation of the weak Cu–O (ether) bonds, loss of the two water molecules and rearrangement of the phenoxy ligands with cross bridging. The insertion of the pyrimidine ligands provides the inherent hydrogen bonding stabilization observed in the structure.

The isomorphism confirmed for crystals of the complex $[Cu_2(PA)_4(2\text{-aminopyrimidine})_2]$ is consistent with the similarity and general structural behaviour of both phenoxyacetic acid and 4-fluorophenoxyacetic acid. The extension of isomorphism to the series of PA and 4-CPA complexes to include those of 4-FPA with the divalent metals Co, Mg, Mn (space group *Pbca*) and Zn, Cd (space group *C*2), is possible with two exceptions, zinc 4-fluorophenoxyacetate and cadmium 4-chlorophenoxyacetate. No reason can be offered at the present time for the anomaly with the zinc 4-FPA complex since both the phenoxyacetic and 4-chlorophenoxyacetic acid complexes are isomorphous [6]. In the case of the $[Cd(4\text{-}CPA)_2(H_2O)_4]$, the larger size of the Cd ion, together with the additional steric effects of the larger chlorine substituent may be contributing factors.

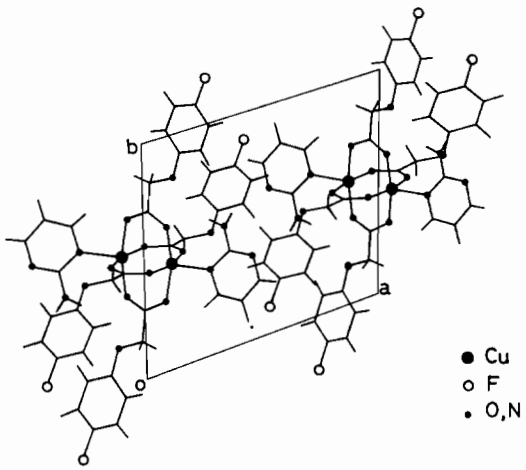

Fig. 4. The packing of (*2*) in the cell viewed perpendicular to *ab*.

Table IV compares the conformational features of the chelated 4-FPA ligands in complex (*1*) with those for the analogous compounds in other $[Cu(phenoxy)_2(H_2O)_2]$ systems, [(phenoxy) = phenoxyacetate [3], 4-methoxyphenoxyacetate [5] and 4-chlorophenoxyacetate [6]].

It is significant to note that the chelate ring system becomes more puckered in proceeding from phenoxyacetate through (*1*) to 4-chlorophenoxyacetate, although the gross conformation of the oxoacetic acid side-chain remains roughly 'planar'. The planar conformation is the one preferred for these acids in the solid state [7]. Paralleling this change is a decrease in the Cu–O(7) (axial) bond distance which proceeds from 2.50, 2.44(1) Å (phenoxyacetate) [3], 2.471(2) Å (4-fluorophenoxyacetate), 2.432(2) Å (4-methoxyphenoxyacetate) [5], to 2.406(4) Å (4-chlorophenoxyacetate) [6]. This represents strengthening of the axial bond which for this series can only arise as a result of the influence of the para-substituent on the phenoxy ring system. The uncomplexed acid in (*1*) has the planar conformation of the (assumed) isostructural phenoxyacetic acid [7], while in the case of the dimeric species (*2*), there is considerable variation in the conformational features of the phenoxyacetate ligands. This is consistent with the observations for other tetracarboxylate bridged dimer species involving phenoxyalkanoic acids [20]. This effect is largely due to packing within the crystal.

TABLE IV. Comparative Torsion Angles (Degrees) within the Chelate Ring for the Copper(II)–phenoxy, 4-fluorophenoxy (*1*), 4-methoxyphenoxy-, and 4-chlorophenoxyacetate Analogues.

	phenoxy*	4-fluoro-	4-methoxy-	4-chloro-
Cu–O(10)–C(9)–C(8)	−8.8, −7.3, +7.2	+10.5	+19.5	−9.9
O(10)–C(9)–C(8)–O(7)	−9.3, −5.9, +9.8	+1.5	−1.7	−16.2
C(9)–C(8)–O(7)–Cu	+17.1, +12.4, −16.5	−8.9	−11.6	+27.3
C(8)–O(7)–Cu–O(10)	−16.9, −12.6, +16.0	+10.6	+15.9	−26.2
O(7)–Cu–O(10)–C(9)	+14.1, +10.8, −12.8	−11.5	−19.2	+19.8
reference	[3]	(this work)	[5]	[6]

* 1.5 molecules per asymmetric unit.

Acknowledgements

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