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Metal–Phenoxyalkanoic Acid Interactions. Part I. Crystal and Molecular Structures of Diaquabis(*p*-chlorophenoxyacetato)copper(II), Diaquabis(phenoxyacetato)zinc(II) and Diaquabis(*p*-chlorophenoxyacetato)zinc(II)

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*The crystal structures of diaquabis(*p*-chlorophenoxyacetato)copper(II) (1) and diaquabis(phenoxyacetato)zinc(II) (2) have been determined by X-ray methods from diffractometer data and refined by least squares to* R *0.059 (1) and 0.032 (2) for 999 and 1472 'observed' reflections respectively. Crystals of (1) are triclinic, space group* $P\bar{1}$ *with* $Z = 1$ *in a unit cell of dimensions* $a = 7.065(3)$, $b = 13.273(11)$, $c = 5.114(2)$ Å, $\alpha = 93.72(5)$, $\beta = 103.64(4)$, $\gamma = 81.63(5)°$. *The complex has a centrosymmetric tetragonally-distorted octahedral stereochemistry, the co-ordination sphere consisting of two water oxygens [Cu–O, 1.960(4) Å] and two carbonyl oxygens [Cu–O, 1.956(4) Å] from different bidentate phenoxyacetate ligands about the square plane while the axial positions are occupied by two ether oxygens [Cu–O, 2.406(4) Å]. The water oxygens are tied into a two-dimensional hydrogen-bonded network involving the un-co-ordinated carboxyl oxygens (O···O, 2.652 Å) and the co-ordinated carboxyl oxygens with the* $O(H_2)\cdots O$ *distances of 2.164 and 2.708 Å respectively. Compound (2) is monoclinic, space group* C2 *with* $Z = 2$ *in a cell of dimensions* $a = 11.625(3)$, $b = 5.221(1)$, $c = 13.767(4)$ Å, $\beta = 101.05(5)°$. *The complex (2) possesses a distorted trapezoidal pyramidal stereochemistry involving two water oxygens [Zn–O, 1.994(1) Å] and four carboxyl oxygens from phenoxyacetate ligands [Zn–O, 2.118(1) Å]. In both structures the phenoxy ligands are essentially planar and have similar distances and angles to those found in the structure of un-co-ordinated phenoxyacetic acid. Single-crystal and powder diffractometer X-ray data are also reported for diaquabis(*p*-chlorophenoxyacetato)zinc(II) (3), which is isostructural with (2).*

Introduction

The phenoxyalkanoic acids constitute an important group of synthetic chemicals which may have either auxin or *anti*-auxin properties, depending on both the position and type of substituent in the benzene ring and on the side-chain configuration. The acetic acid analogues such as 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 4-chloro-2-methylphenoxyacetic acid (MCPA) are common commercial auxin herbicides. Similar herbicidal activity is possessed by the analogous 2-propionic acid homologues, 2,4-DP, 2,4,5-TP and MCPP. Although metal chelate formation has been disproved as the mode by which the phenoxy herbicides act [1], interaction of phenoxyalkanoic acids with common metal ions is of particular interest in relation to a basic understanding of their scavenging effect in aqueous media. Furthermore, the crystal structures of 14 phenoxyalkanoic acids, both herbicidally active and inactive are now known [2–7] so that a comparison of the conformational aspects of the co-ordinated and un-co-ordinated ligands is possible. The effect of ring substitution and the nature of the side-chain on complex stereochemistry and on the mode of complexation with different metal types may also become more predictable.

Previous studies of metal phenoxy complexes have involved primarily copper(II) in relation to magnetic properties. Using X-rays, Prout and co-workers have characterised several phenoxyacetic acid complexes: diaquabis(phenoxyacetato)copper(II) [8], aquabis(phenoxyacetato)bis(pyridine)copper(II) [9], bis(phenoxyacetato)copper(II) [10], diaquabis(*p*-methoxyphenoxyacetato)copper(II) [11], diaquabis(*p*-methoxyphenoxyacetato)copper(II) dihydrate

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[11], tetraaquabis(phenoxyacetato)nickel(II) [12] and sodium phenoxyacetate hemi-hydrate [13]. The diaqua complexes mainly involve *trans*-waters and bidentate phenoxy ligands bonding *via* the ether oxygen and a carboxyl oxygen except for the dihydrate which is four-co-ordinate with monodentate *p*-methoxyphenoxy ligands. Another copper phenoxyacetate, the square pyramidal triaquabis(phenoxyacetato)copper(II), involving monodentate phenoxy ligands is also known [14].

In the present series there is no evidence of the carboxyl bridged dimer of the type M_2(carboxylate)$_4$-(L)$_2$ which was found in only a small number of aromatic carboxylic acid complexes of copper(II), *e.g.* copper(II) *o*-bromobenzoate [15], and copper(II) aspirinate [16], or the water-carboxylate bridged polymer copper(II) benzoate trihydrate [17]. The only exception is the case of anhydrous copper(II) phenoxyacetate complex [10], which has both chelate bridging and monodentate bridging ligands forming a complex hexamer.

There is a dearth of structural information on zinc(II) complexes of aromatic or aromatic-aliphatic acids. Diaquabis(salicylato)zinc(II) [18], and diaquabis(thiobenzoato)zinc(II) [19] represent two examples of the somewhat rare tetrahedral stereochemistry involving two aqua ligands and two monodentate carboxylic acids. Another tetrahedral aromatic acid complex, zinc *o*-ethoxybenzoate hydrate [20], has a bridging carboxylate as well as monodentate carboxylate oxygens and one water in the co-ordination sphere. This paper reports the crystal and molecular structures of diaquabis(*p*-chlorophenoxyacetato)copper(II), diaquabis(phenoxyacetato)zinc(II) and the crystal data for diaquabis(*p*-chlorophenoxyacetato)zinc(II).

Experimental

Preparation of Complexes

Complexes were prepared by reaction of a solution of the phenoxyalkanoic acid in hot aqueous ethanol with excess metal carbonate. After removal of the unreacted carbonate, the crystals were allowed to grow from the diluted solution. With (*2*) and (*3*), crystals suitable for single crystal X-ray analysis were obtained as colourless needles by cooling the solution in ethanol/water slowly over a number of days in a Dewar flask. Pale blue needle-shaped crystals of (*1*) were readily obtained by slow crystallization as only one crystal modification, in contrast to the copper(II) complexes of phenoxyacetic acid, *o*-chlorophenoxyacetic acid and 2,4-dichlorophenoxyacetic acid where up to three forms, having from 0 to 4 waters per formula unit, are known.

Anal. Found for (*1*): C, 40.8; H, 3.50; Cl, 15.0; Cu, 13.6%. Calcd. for $C_{16}H_{16}Cl_2CuO_8$: C, 40.8; H, 3.42; Cl, 15.1; Cu, 13.5%. Found for (*2*): C, 47.0; H, 4.64; Zn, 16.5%. Calcd. for $C_{16}H_{18}O_8Zn$: C, 47.6; H, 4.47; Zn, 16.2%. Found for (*3*): C, 40.2; H, 3.49; Cl, 14.8; Zn, 13.8%. Calcd. for $C_{16}H_{16}Cl_2O_8Zn$: C, 40.7; H, 3.41; Cl, 15.0; Zn, 13.8%.

X-ray Data

a) *Single crystal diffractometry*

Data for (*1*) were collected on a Syntex P2$_1$ four-circle diffractometer at the Institute for Cancer Research, Philadelphia, Pa., U.S.A. A single crystal with dimensions 0.12 × 0.15 × 0.25 mm, mounted about the *c* (prism) axis was used and 1215 reflections, with 999 having $I > 2.5\sigma(I)$ were considered observed up to a $2\theta_{max}$ = 50°. For (*2*), data were collected using a Nonius CAD-4 four-circle diffractometer. 1472 reflections with $I > 2.5\sigma(I)$ were considered observed of 1571 independent reflections collected up to $2\theta_{max}$ = 64° using the $\omega/2\theta$ mode from a single crystal measuring 0.40 × 0.20 × 0.20 mm. In each case, graphite monochromated Mo-Kα radiation was used and no significant change was observed in the intensities of three standards monitored during data collection.

b) *Powder diffractometry*

X-ray powder diffractometer data were obtained on a Philips model PW1140 diffractometer using crystal monochromated Co-Kα radiation (λ = 1.7889 Å). Intensities for (*2*) were correlated with those from the single crystal data and indexed. The approximate single crystal cell parameters for (*3*) obtained from Weissenberg photography were used to index the diffractometer data. More accurate cell parameters were then calculated using least-squares from data up to $2\theta_{max}$ = 40°.

Crystal Data

(*1*) $C_{16}H_{16}Cl_2CuO_8$, *M* = 470.4, Triclinic *a* = 7.065(3), *b* = 13.273(11), *c* = 5.114(2) Å, α = 93.72(5), β = 103.64(4), γ = 81.63(5), *U* = 460.8 Å^3, *Dm* = 1.68 (by flotation), *Z* = 1, *Dc* = 1.70, *F*(000) = 239, Mo-Kα radiation, λ = 0.7107 Å; μ(Mo-Kα) = 15.6 cm^{-1}. Space group $P\bar{1}(C_i^1$, No. 2).

(*2*) $C_{16}H_{18}O_8Zn$, *M* = 403.4, Monoclinic, *a* = 11.625(3), *b* = 5.221(1), *c* = 13.767(4) Å, β = 101.05(5)°, *U* = 820.1 Å^3, *Dm* = 1.62 (by flotation), *Z* = 2, *Dc* = 1.64, *F*(000) = 416. Mo-Kα radiation, λ = 0.7107 Å; μ(Mo-Kα) = 15.9 cm^{-1}. Space group $C2(C_2^3$, No. 5) from systematic absences and successful structure solution and refinement.

(*3*) $C_{16}H_{16}Cl_2O_8Zn$, *M* = 473.2, Monoclinic, cell parameters (powder diffractometer data) *a* = 11.64 (1), *b* = 5.21(1), *c* = 15.42(2) Å, β = 100.8(1)°, *U* = 919 Å^3, *Dm* = 1.66 (by flotation), *Dc* = 1.71. Space group *C*2 (from systematic absences).

Structure Solution

Both structures (*1*) and (*2*) were solved by the heavy atom method.

Full matrix least-squares refinement with all non-hydrogen atoms anisotropic gave a final $R\,[=\Sigma||F_o - F_c||/\Sigma F_o]$ of 0.059(*1*) and 0.032(*2*) and $Rw\,[=(\Sigma w||F_o - F_c||^2/\Sigma w|F_o|^2)^{1/2}]$ of 0.072(*1*) and 0.034(*2*). Neither data set was corrected for absorption. Scattering factors were those of the neutral atoms [21, 22] while the metal ions were corrected for anomalous dispersion [23]. Hydrogen positions were located in difference-Fourier syntheses and included in the refinement at fixed positions with the value of their isotropic U set invariant at 0.05 Å^2. The crystallographic programme set SHELX was used [24]. With (*1*), no extinction corrections were made but for (*2*), four intense low-angle reflections (001, $1\bar{1}2$, $\bar{2}01$, $\bar{2}02$) were considered to be seriously affected by extinction and were removed before the final cycle of refinement. Structure amplitudes and anisotropic thermal parameters are listed in Supplementary Publication.

Final positional parameters are given in Table I. The atom naming scheme used for the phenoxyacetic acid ligands follows the convention previously employed for the structures of the phenoxyalkanoic acids [2]. This is illustrated in Figs. 1 and 2 [the complexes (*1*) and (*2*) respectively] and in Fig. 3, which compares the bond distances and angles within the phenoxy ligands.

Discussion

(a) *Diaquabis(p-chlorophenoxyacetato)copper(II) (1)*

The structure of diaquabis(*p*-chlorophenoxyacetato)copper(II) consists of centrosymmetric *trans* related bis-chelate phenoxyacetate ligands about the copper(II) ions (Fig. 1). This is very similar to that

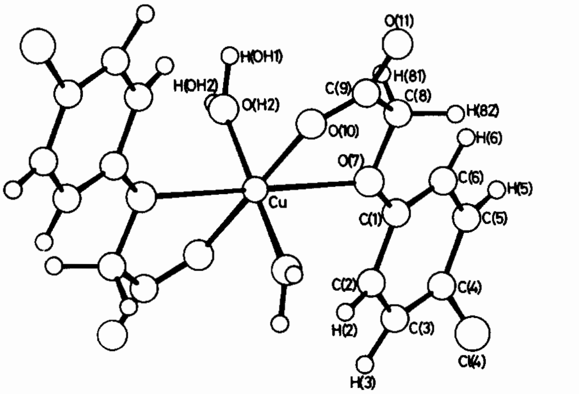


Fig. 1. Molecular configuration and naming scheme for diaquabis(*p*-chlorophenoxyacetato)copper(II) (*1*).

TABLE I. Atomic Positional Parameters (×10^4) with Estimated Standard Deviations in Parentheses. The Atom Numbering Scheme within the Ligands is the One Used for the Phenoxyalkanoic Acid Series [2].

(*1*) Diaquabis(*p*-chlorophenoxyacetato)copper(II)				(*2*) Diaquabis(phenoxyacetato)zinc(II)			
Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Cu	0	0	0	Zn	0	0	0
O(H2)	2177(8)	–437(5)	3033(10)		–761(2)	–2607(5)	727(2)
C(1)	–226(11)	2447(6)	2967(16)		2267(2)	8275(5)	2823(2)
C(2)	–2179(11)	2389(7)	3013(19)		1636(2)	9906(10)	3348(2)
C(3)	–3076(13)	3062(8)	4686(23)		2225(3)	11664(7)	3999(2)
C(4)	–2022(13)	3770(7)	6229(18)		3438(3)	11902(7)	4141(2)
C(5)	–112(13)	3840(8)	6204(18)		4049(3)	10351(7)	3614(2)
C(6)	800(12)	3162(7)	4535(18)		3476(2)	8523(6)	2946(2)
O(7)	528(9)	1732(4)	1266(12)		1611(1)	6545(4)	2209(1)
C(8)	2467(9)	1818(6)	909(15)		2249(2)	4874(9)	1700(1)
C(9)	2900(9)	1035(6)	–1273(14)		1456(2)	2935(5)	1106(2)
O(10)	1886(7)	302(4)	–1996(10)		371(2)	2833(4)	1118(1)
O(11)	4296(7)	1166(5)	–2245(12)		1911(2)	1438(5)	582(1)
Cl(4)	–3184(4)	4628(2)	8306(6)		–	–	–
H(2)	–3234	2066	1413		800	10019	3246
H(3)	–4416	2879	5118		1769	12797	4350
H(4)	–	–	–		3865	13305	4711
H(5)	757	4311	7556		4971	10258	3723
H(6)	2041	3287	4306		4049	7442	2469
H(81)	3552	1626	2653		2797	4282	2162
H(82)	2594	2585	416		2657	5307	1227
H(OH1)	3657	–540	3193		–525	–4074	1084
H(OH2)	2313	–379	4569		–	–	[a]

[a] Not located.

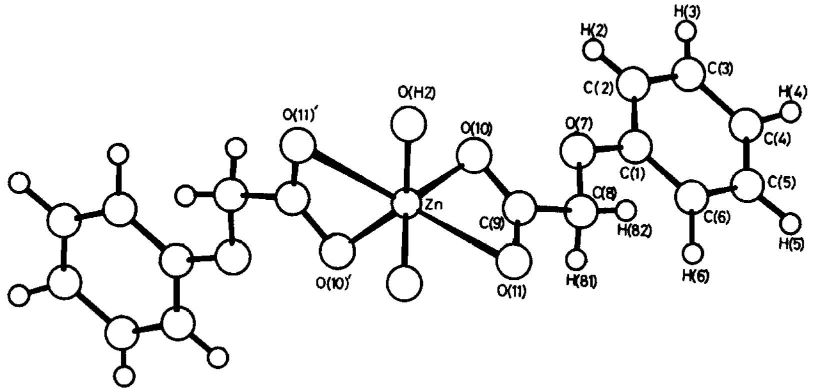
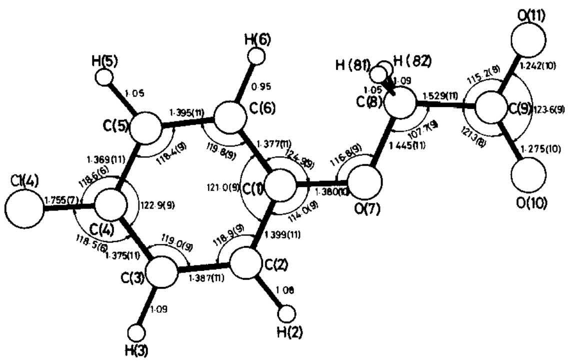
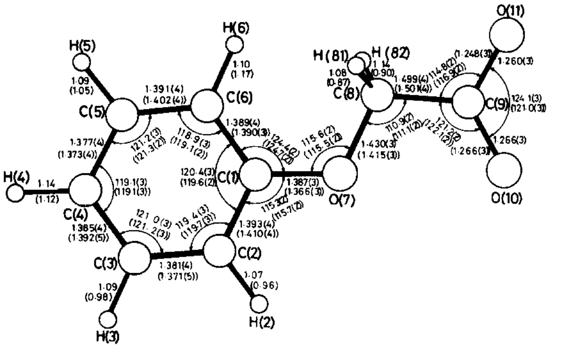


Fig. 2. Molecular configuration and naming scheme for diaquabis(phenoxyacetato)zinc(II) (*2*).



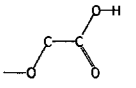
(a) Diaquabis(*p*-chlorophenoxyacetato)copper(II) (*1*).



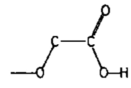
(b) Diaquabis(phenoxyacetato)zinc(II) (*2*).

Fig. 3. Comparative bond distances and angles within the phenoxyacetato ligand in (a) (*1*) and (b) (*2*). Figures in parentheses in (b) are the values for un-co-ordinated phenoxyacetic acid [3].

found for diaquabis(*p*-methoxyphenoxyacetato)copper(II) and diaquabis(*p*-nitrophenoxyacetato)copper(II) [11] and diaquabis(phenoxyacetato)copper(II) [8]. The similarity to the *p*-methoxyphenoxyacetate complex is carried through to the volume of the triclinic cell [486 *vs* 461 Å^3 (this structure)] and the packing of the complex units in the cell. The co-ordination sphere involves two carbonyl oxygens [1.956(4) Å], two oxygens from water ligands [1.960(4) Å] and two more distant ether oxygens [2.406(4) Å] in the axial positions (Table IIa). These distances compare with the corresponding distances 1.955, 1.945 and 2.432 Å in both the *p*-methoxyphenoxy and phenoxy complexes. The phenoxy ligands are essentially planar, which is similar to the conformation found for the free acid [3]. Intraligand distances and angles are given in Fig. 3 and are compared with those for phenoxyacetic acid and for the ligands in diaquabis(phenoxyacetato)zinc(II) (*2*). The *synplanar syn-syn* (carbonyl) (s-s) conformation, which is found with few exceptions in structures of the free phenoxyalkanoic acids [2] is also found in the bonded ligand.



syn-syn (s-s) conformation



syn-anti (s-a) conformation

This conformation places the ether oxygen O(7) and the bonded carbonyl oxygen O(10) 2.668 Å apart, which is comparable to 2.671 Å for phenoxyacetic acid and 2.685 Å for the mean of 6 free acids [2]. This bonding mode *via* carbonyl oxygens has been proposed previously by Klug and Alexander [18] to explain the mode of bonding in the complex diaquabis(salicylato)zinc(II) and also in ammonium hydrogen disalicylate hydrate [25], on the basis of the C–O (carbonyl) and C–O (hydroxyl) bond lengths in the carboxyl group, 1.19, 1.26 Å respectively. In the free aromatic carboxylic acids, these distances become equi-dimensional as the proton is lost or delocalised. This phenomenon is usually also accompanied by a tendency in the C–C–O angles to become more trigonal [26, 27]. In the zinc salicylate

TABLE II

a) Distances (Å) and angles (°) about the co-ordination sphere for (1) and (2).

Distances

(*1*)		(*2*)	
Cu–O(H2)	1.960(4)	Zn–O(H2)	1.994(1)
Cu–O(10)	1.956(4)	Zn–O(10)	2.118(1)
Cu–O(7)	2.406(4)	Zn–O(11)	2.337(1)

Angles

O(H2)–Cu–O(10)	89.8(3)	O(H2)–Zn–O(10)	99.2(1)
O(H2)–Cu–O(7)	88.2(3)	O(H2)–Zn–O(10)′	142.5(1)
O(7)–Cu–O(10)	74.6(3)	O(H2)–Zn–O(H2)′	93.9(1)
Cu–O(7)–C(8)	105.8(4)	O(10)–Zn–O(10)′	91.4(1)
Cu–O(10)–C(9)	121.6(4)	O(10)–Zn–O(11)	58.6(1)
		O(10)–Zn–O(11)′	84.7(1)
		O(11)–Zn–O(H2)	122.1(1)

b) Comparative torsion angles (°) in the oxoacetic acid residue for (1), (2) and un-co-ordinated phenoxyacetic acid.

Compound	Angle		
	C(2)–C(1), O(7)–C(8)	C(1)–O(7), C(8)–C(9)	O(7)–C(8), C(9)–O(10)
(*1*)	−173.7	+173.7	−16.2
(*2*)	−178.0	+175.9	+3.7
phenoxyacetic acid	−175.1	+176.1	−0.9

complex, these angles are almost equal (118, 120°). Among the free phenoxyalkanoic acids, the C–O bond lengths become increasingly equivalent with delocalisation of the acid group, with the C–C–O angles remaining recognizable as involving carbonyl or hydroxyl oxygens. This allows a classification of the conformational motif as either *synplanar* [*s-s*(carbonyl)] or *synplanar* [*s-a*(carbonyl)]. The *s-s* motif is adopted with only one exception (*o*-chlorophenoxyacetic acid) [7] among the phenoxyacetic acids although both phenoxyisobutyric acid and *p*-chlorophenoxyisobutyric acid [4] have the *s-a* conformation.

On the basis of the angles about the carboxyl groups for the phenoxyacids, bonding may be determined as involving either the carbonyl oxygen or the hydroxyl oxygen (Table III), those involving carbonyl predominating. From the structural information available for 13 phenoxyacids [2–5], the C–C–O (carbonyl) angle [range 119.3–128.7° (mean 123.3°)] is always significantly greater than the C–C–O (hydroxyl) angle [range 111.9–116.6, (mean 113.7°)]. In all cases when the proton has been located, it has been used to label the hydroxyl oxygen. In both compounds [(*1*) and (*2*)] the phenoxyacetate ligand retains the *s-s* conformation and bonding involves the carbonyl oxygen *not* the hydroxyl oxygen as might be expected. Table III lists the distances and angles and the conformational motifs suggested for the carboxylic acid groups for all known copper phenoxy complexes. These findings of course obviate most assumptions about the bonding mode in carboxylates as involving exclusively the hydroxyl oxygen bonding to the metal. For example, the two molecules of triaquabis(phenoxyacetato)copper(II) [14] in the asymmetric unit have both carbonyl and hydroxyl oxygens bonded to the metal. It is considered that the C–C–O angles are less prone to change from their free acid values than the C–O distances while the conformational change from *synplanar s-s* to *s-a* does not normally occur. There is a strong tendency for the phenoxys so far analysed to adopt the same preferred planar conformation in the free as in the complexed state. Torsion angles about the oxoacetic acid residue for (*1*) and (*2*) are compared in Table IIb.

In the examples where C–C–O angles (involving carbonyl and hydroxyl oxygens) are the same, within experimental error, preference would be given to the *s-s* conformation if that was the natural conformation in the uncomplexed state.

Packing in the unit cell is shown in Fig. 4. The molecules are stabilized in the *a* direction by a hydrogen bonding network involving the waters and the unbonded oxygens [O(11)] of carboxylic acid groups from different complex units with an O···O dis-

TABLE III. Comparative C–O Distances (Å), C–C–O Angles (°) and Bonding Modes for the Carboxylic Acid Groups in Phenoxyacetic Acid Complexes. (*x*) Indicates a Bonded Oxygen; *m* = Monodentate; *b* = Bidentate. A and B Represent Separate Molecules in the Asymmetric Unit while (i) and (ii) are the Independent Phenoxy Ligands.

Complex	C–O (carbonyl)	C–O[a] (hydroxyl)	$\mathrm{C{-}C}\overset{\mathrm{O}}{\diagup}$ (carbonyl)	$\mathrm{C{-}C}\overset{\mathrm{O}}{\diagup}$ (hydroxyl)	Motif	Bonding mode	Ref.
Cu(phenoxy)$_2$(H$_2$O)$_2$	A 1.28(2) (*x*)	1.26(2)	121.5(12)	117.6(12)	*syn–syn*	*m*(carbonyl)	8
	B(i) 1.27(2) (*x*)	1.24(2)	122.4(12)	116.4(12)	*syn–syn*	*b*(carbonyl), ether)	
	(ii) 1.29(2) (*x*)	1.26(2)	121.3(12)	117.3(12)	*syn–syn*		
Cu(phenoxy)$_2$(H$_2$O)$_3$	A(i) 1.23(2) (*x*)	1.25(2)	120(2)	113(2)	*syn–syn*	*m*(carbonyl)	9
	(ii) 1.20(2)	1.33(2) (*x*)	123(2)	113(2)	*syn–syn*	*m*(hydroxyl)	
	B(i) 1.23(2) (*x*)	1.25(2)	122(2)	115(2)	*syn–syn*	*m*(carbonyl)	
	(ii) 1.22(2)	1.31(2) (*x*)	124(2)	113(2)	*syn–syn*	*m*(hydroxyl)	
Cu(phenoxy)$_2$	(i) 1.27(2) (*x*)	1.23(2) (*x*)	117(2)	116(2)	*syn–syn*	*b*(bridging carboxyl)	10
	(ii) 1.26(2) (*x*)	1.21(2) (*x*)	122(2)	114(2)	*syn–syn*	*b*(carbonyl, ether + carbonyl bridge)	
Cu(*p*-chlorophenoxy)$_2$(H$_2$O)$_2$	1.275(10) (*x*)	1.242(10)	121.3(8)	115.2(8)	*syn–syn*	*b*(carbonyl, ether)	This work
Cu(*p*-methoxyphenoxy)$_2$(H$_2$O)$_2$	1.264(5) (*x*)	1.237(5)	121.1(3)	114.3(3)	*syn–syn*	*b*(carbonyl, ether)	11
Cu(*p*-methoxyphenoxy)$_2$(H$_2$O)$_2$·2H$_2$O	1.22(2)	1.30(2) (*x*)	117(1)	117(1)	*syn–syn*	*m*(hydroxyl)	11

[a] The hydroxyl oxygen is defined as having angle C–C–O < 120°. Where both C–C–O angles are equal, assignment is made on the basis of preferred conformation.

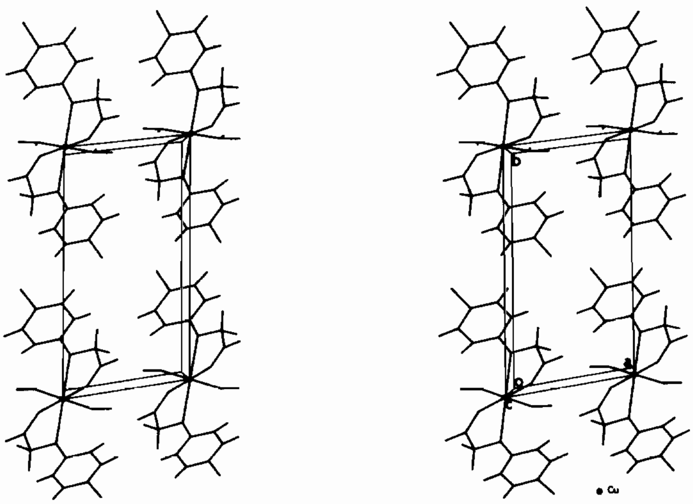


Fig. 4. Stereoview of the packing of (*1*) in the cell viewed perpendicular to the *ab* plane.

tance of 2.652 Å. The bonded oxygen [O(10)] is also involved in a short intermolecular contact with a water oxygen (2.708 Å) while stability within the complex unit is achieved by close intramolecular contacts of O(10) with O(H2) (2.764 Å) and the centrosymmetrically related O(H2)′ (2.775 Å).

(b) *Diaquabis(phenoxyacetato)zinc(II) (2)*

The complex units of diaquabis(phenoxyacetato)-zinc(II) (*2*) have a distorted octahedral stereochemistry, the co-ordination sphere consisting of two oxygens from water molecules [Zn–O, 1.994(1) Å] and four oxygens from asymmetric carboxylate groups [Zn–O, 2.118(1); 2.337(1) Å] (Fig. 2) with the zinc lying on the crystallographic two-fold rotational axis. This is similar to the systems found for diaquabis(salicylato)zinc(II) [18] and diaquabis(thiobenzoato)zinc(II) [19]. Distances and angles about the co-ordination sphere and within the phenoxyacetate ligand are shown in Table IIa and Fig. 3. It is particularly significant that the intra-ligand distances and angles are similar to those found for the un-co-ordinated phenoxyacetic acid [6]. The ligand in (*2*) also has the *synplanar (s-s)* conformation found for diaquabis(*p*-chlorophenoxyacetato)copper(II) (*1*). The Zn–O(H2) distance (1.994(1) Å) is shorter than the values for the salicylate complex (2.06 Å), the thiobenzoate complex (2.03 Å) and for most recent reported zinc structures involving water in the co-ordination sphere (Table IV). However it is not considered abnormal when compared with the range of 1.92–2.10 Å [28]. In the 'tetrahedral' Zn(*o*-ethoxybenzoato)(H_2O) complex [20], the Zn–OH_2 distance (1.988 Å) is very similar to that for (*2*) and moreover these two complexes have certain common features within the co-ordination sphere. Whereas in (*2*) the molecules comprise discrete hydrogen bonded units, the *o*-ethoxybenzoate complex sphere consists of one water and two carboxylate ligands, one monodentate and the other bidentate, bridging two complex units. The anomalous feature of the present structure and that of the ethoxybenzoate is the extreme distortion of the angles about Zn involving O(H2) and O(10) [142.4 and 148.0° respectively] if tetrahedral stereochemistry is assumed. Although the Zn–O(10) distance is acceptable in both compounds [2.118, 2.054 Å respectively], the C(8)–C(9) and C(9)···Zn vectors are almost colinear [C(8)–C(9)···Zn angle, 174.4 and 172.4° respectively, Fig. 5a], while the angles involving O(H2) and C(9)

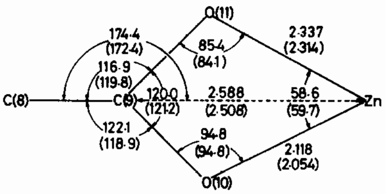


Fig. 5a. Comparative dimensional features of the bonding of carboxylate ligands about Zn in complex (*2*) and in Zn (*o*-chlorobenzoato)$_2$(H_2O) (in parentheses).

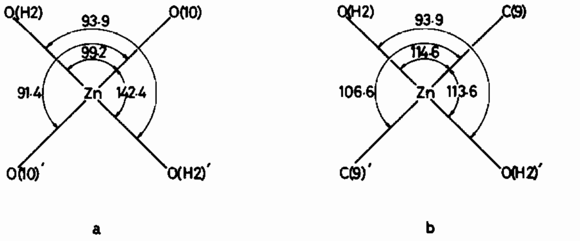


Fig. 5b. Comparison of the angles about the co-ordination sphere for (*2*) involving: (a) the carbonyl and aqua ligands and (b) the 'line of centre' approach *via* the carboxylate group [31].

TABLE IV. Comparative Zn–OH_2 and Other Zn–O Mean Distances (Å) for a Number of Recent Structures Having Aqua Ligands in the Co-ordination Sphere. Where a Significant Disparity Exists in the Distances, a Range is Indicated.

Complex	Stereochemistry	Zn–OH_2	Zn–O	Ref.
$Zn(phenoxyacetato)_2(H_2O)_2$	$Zn(O)_2(OH_2)_2$	1.99	2.12	This work
$Zn(thiobenzoato)_2(H_2O)_2$	$Zn(S)_2(OH_2)_2$	2.03	–	a
$Zn(NO_3)_2 \cdot 2H_2O$	$Zn(O)_4(OH_2)_2$	2.04	2.10–2.17	b
$Zn(edta) \cdot 6H_2O$	$Zn(OH_2)_4$, $Zn(N_2O_4)$	2.10	2.07	c
$Zn(OH_2)_6 \cdot SiF_6$	$Zn(OH_2)_6$	2.08	–	d
$Zn(NO_3)_2 \cdot 2Hg(CN)_2 \cdot 7H_2O$	$Zn(N)_2(OH_2)_4$	2.11	–	e
$Zn(NO_3)_2 \cdot 2Hg(CN)_2 \cdot 7H_2O$	$Zn(N)_2(OH_2)_4$	2.106	–	f
$Zn(trien)(Cl_2)(H_2O)$	$Zn(Cl)(N)(O)_3(OH_2)$	2.19	2.14	g
$Zn(oxamido)_2(H_2O)_2$	$Zn(O)_4(OH_2)_2$	2.09	2.04–2.15	h
$Zn(isonicotinato)_2(H_2O)_4$	$Zn(N)_2(H_2O)_4$	2.09, 2.16	–	i
$K_2Zn(H_2O)_6(SO_4)_2$	$Zn(OH_2)_6$	2.032–2.133	–	j
$Zn(2\text{-}pyridylacetato)(H_2O)_2$	$Zn(N)_2(O)_2(OH_2)_2$	2.21	2.08	k
$Zn(2\text{-}ethoxybenzoato)(H_2O)_2$	$Zn(O)_3(OH_2)$	1.99	2.06	l
$Zn(purpurato)_2(H_2O)_2(NO_3)$	$Zn(ONO)(O)_2(OH_2)_2$	2.01–2.14	2.10, 2.13	m
$Zn(OH_2)_6 \cdot (C_4HO_2)_2$ (1:1)	$Zn(OH_2)_6$	2.09	–	n
$Zn(formato)_2(H_2O)_2$	$Zn(O)_6 \cdot Zn(O_2)(OH_2)_4$	2.05–2.10	2.07–2.17	o
$Zn(0.5)Cu(0.5)(formato)(H_2O)_2$	$Zn(O)_4(OH_2)_2$	2.10	2.02–2.10	p
$Zn(malato)(H_2O)_2 \cdot H_2O$	$Zn(O)_4(OH_2)_2$	2.11	2.05–2.15	q
$Zn(thioglycollato)(H_2O)_3 \cdot H_2O$	$Zn(OSO)(OH_2)_3$	2.05–2.10	2.03–2.10	r

[a] M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *J. Chem. Soc. Dalton*, 67 (1976). [b] D. Petrovic and B. Ribar, *Acta Cryst., B31*, 1795 (1975). [c] A. I. Pozhiaev, T. N. Polynova, M. A. Porai-Koshits and J. Neronova. *J. Struct. Chem., 14*, 527 (1973). [d] S. Ray, A. Zalkin and D. H. Templeton, *Acta Cryst., B29*, 2741 (1973). [e] C. Mahon, *Inorg. Chem., 10*, 1813 (1971). [f] L. F. Power, J. A. King, F. H. Moore, *J. Chem. Soc. Dalton*, 2072 (1975). [g] H. Follner, *Z. Anorg. Chem., 43*, 387 (1972). [h] A. Braibanti, M. A. Pellinghelli, A. Tiripicchio and M. Tiripicchio-Camellini, *Acta Cryst., B27*, 1240 (1971). [i] M. B. Cingi, A. G. Manfredotti, C. Guastini, A. Musatti and M. Nardelli. *Gazzetta, 101*, 815 (1971). [j] J. Whitnall, C. H. L. Kennard, J. Nimmo and F. H. Moore, *Cryst. Struct. Comm., 4*, 717 (1975). [k] R. Faure and H. Loiseleur, *Acta Cryst., B28*, 811 (1972). [l] S. Natarajan, Doddahalli S. Sake Gowda and L. Cartz, *Acta Cryst., B30*, 401 (1974). [m] A. H. White and A. C. Willis, *J. Chem. Soc. Dalton*, 1377 (1977). [n] M. P. Gupta and J. L. Agrawal. *Cryst. Struct. Comm., 6*, 103 (1977). [o] N. Burger and H. Fuess, *Z. Krist., 145*, 346 (1977). [p] T. Ogata, T. Taga and K. Osaki, *Bull. Chem. Soc. Japan, 50*, 1680 (1977). [q] A. T. Reed and A. Karipades, *Acta Cryst., B32*, 2085 (1976). [r] M. G. B. Drew, D. A. Rice and C. W. Timewell, *J. Chem. Soc. Dalton*, 144 (1975).

of the carboxylate groups are closer to the normal tetrahedral value (Fig. 5b). The second carboxyl oxygen [O(11)] of (*2*) is slightly more distant from the zinc [2.337(1) Å], consistent with the smaller C(8)–C(9)–O(11) angle associated with the hydroxyl oxygen in all free phenoxyalkanoic acids [2] and benzoates [25]. Although the asymmetric carboxylate group has not been previously considered in bonding modes in metal carboxylates its existence is recognized in this example.

An analogous case to this one involves an asymmetric bidentate nitrato group in the seven-co-ordinate complex diaquanitrato(purpurato)zinc(II) hydrate [29] which has unequal long Zn–O(nitrate) distances of 2.266 and 2.511 Å. The latter distance is suggestive of a unidentate bonding mode. A similar system exists for the isostructural cobalt(II) complex [29] which has Co–O(nitrate) distances of 2.254 and 2.384 Å. The isostructural series $M(NO_3)_2(py)_3$ exhibits the same trend with M–O asymmetry which decreases in the order Cu $\gg$ Zn $>$ Co, with nitrate bonding in the copper compound approximating to a unidentate mode [30]. In the Zn analogue, Zn–O, distances are 2.232 and 2.418 Å. Although in the nitrato examples, the authors preferred the bidentate nitrate [29], these structures could also be rationalised on the basis of a square based pyramid, the nitrates occupying single co-ordination positions using a similar 'line of centre' approach [31] as considered in compound (2).

However, Kepert [32] has shown, using repulsion energy calculations, that in complexes of the type $[M(bidentate)_2(unidentate)_2]^{2+}$, with small 'normalised bite' (*b*), distortion of the six-co-ordinate *trans*-octahedral structure to the skew-trapezoidal bipyramidal structure occurs. Similar, though rare examples exist among dimethyltin complexes *e.g.* $[Sn(NO_3)_2(Me)_2]$ which possess asymmetry in the M–O bond length and have comparable *b* values 0.99(2) *cf.* 0.92 in the preceding example. The structure of (*2*) and those of zinc salicylate dihydrate and zinc *o*-ethoxybenzoate hydrate could therefore be described best as having skew-trapezoidal stereochemistries irrespective of the rationale of mode of bonding.

The packing of (*2*) is illustrated in Fig. 6. An intermolecular hydrogen bonding network links the

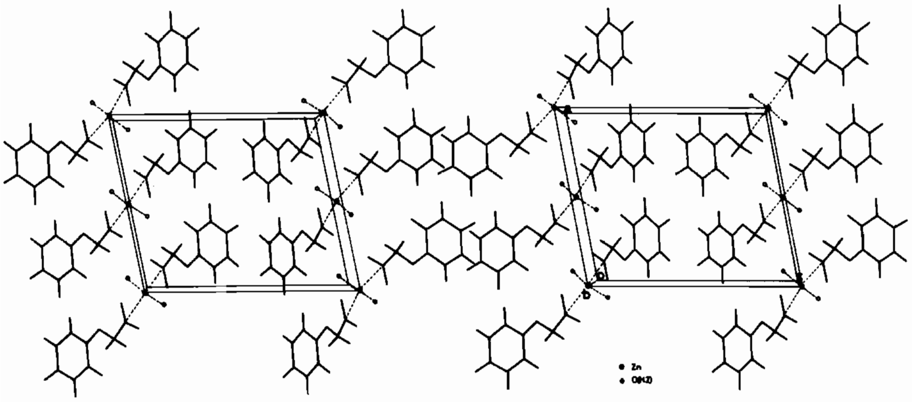


Fig. 6. Stereoview of the packing of (*2*) in the cell viewed perpendicular to the *ac* plane.

oxygens of the water molecules to both carbonyl and hydroxyl oxygens [O(H2)•••O(10), 2.724 Å; O(H2)•••O(11), 2.721 Å] while longer contacts exist between O(H2) and O(11)(2.928 Å) and another water (2.915 Å). No short intramolecular (O•••O) contacts involving O(H2) are present.

(c) *Diaquabis(*p*-chlorophenoxyacetato)zinc(II)* (*3*)

Elemental analysis of (*3*) is consistent with Zn(*p*-chlorophenoxyacetate)(H_2O)$_2$. Single crystal and powder diffractometer X-ray data confirm that (*2*) and (*3*) are isostructural. Indexed powder diffractometer intensities for both compounds are deposited in Appendix 2 as supplementary material. Accommodation of the *p*-chloro substituent in the benzene ring of the phenoxy ligands of (*3*) is achieved by an elongation of the *c* cell dimension (13.767 to 15.42 Å) with only slight changes in *a*, *b* and *β*.

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References

1 D. D. Perrin, *Nature, 191,* 253 (1961).
2 G. Smith and C. H. L. Kennard, *J. Agr. Food Chem., 27,* 779 (1979).
3 C. H. L. Kennard, G. Smith and A. H. White, *Acta Cryst.,* (1980), submitted.
4 G. Smith, C. H. L. Kennard and A. H. White, *Acta Cryst.,* (1980), in the press.
5 G. Smith, C. H. L. Kennard, A. H. White and P. G. Hodgson, *Acta Cryst., B36,* 992 (1980).
6 K. Kozlowska and Z. Galdecki, *Acta Cryst., A34,* S116, 05.3-43 (1978).
7 K. Chandrasekhar and V. Pattabhi, *Acta Cryst., B33,* 1257 (1977).
8 C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust and F. J. C. Rossotti, *J. Chem. Soc. A,* 2791 (1968).
9 C. K. Prout, M. J. Barrow and F. J. C. Rossotti, *J. Chem. Soc. A,* 3326 (1971).
10 J. R. Carruthers, C. K. Prout and F. J. C. Rossotti, *Acta Cryst., B31,* 2044 (1975).
11 C. K. Prout, P. J. Grove, B. D. Harridine and F. J. C. Rossotti, *Acta Cryst., B31,* 2047 (1975).
12 C. K. Prout, C. Walker and F. J. C. Rossotti, *J. Chem. Soc. A,* 556 (1971).
13 C. K. Prout, R. M. Dunn, O. J. R. Hodder and F. J. C. Rossotti, *J. Chem. Soc. A,* 1986 (1971).
14 C. V. Goebel and R. J. Doedens, *Inorg. Chem., 10,* 2607 (1971).
15 W. Harrison, S. Rettig and J. Trotter, *J. Chem. Soc. A,* 1852 (1972).
16 L. Manojlovic-Muir, *Chem. Commun.,* 1057 (1967); *Acta Cryst., B29,* 2033 (1973).
17 H. Koizumi, K. Osaki and T. Watanabé, *J. Phys. Soc. Japan, 18,* 117 (1963).
18 H. P. Klug, L. E. Alexander and G. Gardner-Sumner, *Acta Cryst., 11,* 41 (1958).
19 M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *J. Chem. Soc. Dalton,* 67 (1976).
20 S. Natarajan, Doddahalli S. Sake Gowda and L. Cartz, *Acta Cryst., B30,* 401 (1974).
21 P. A. Doyle and P. S. Turner, *Acta Cryst., A24,* 390 (1968).
22 R. F. Stewart, E. R. Davidson and W. J. Simpson, *J. Chem. Phys., 42,* 3175 (1965).
23 D. T. Cromer and D. Liberman, *J. Chem. Phys., 53,* 1891 (1970).
24 G. M. Sheldrick, SHELX 76. Program for crystal structure determination, Univ. of Cambridge, England, (1976).
25 T. C. Downie and J. C. Speakman, *J. Chem. Soc. A,* 787 (1954).
26 L. Leiserowitz, *Acta Cryst., B32,* 775 (1967).

27 D. A. Dieterich, I. C. Paul and D. Y. Curtin, *J. Am. Chem. Soc., 96,* 6372 (1974).

28 'Molecular Structures and Dimensions', Vol. A1, (1972), *Int., U. of Cryst.,* 59.

29 A. H. White and A. C. Willis, *J. Chem. Soc. Dalton,* 1377 (1977).

30 A. F. Cameron, D. W. Taylor and R. H. Nuttall. *J. Chem. Soc. Dalton,* 1603 (1972).

31 J. G. Bergman and F. A. Cotton, *Inorg. Chem., 5,* 1208 (1966).

32 D. L. Kepert, in *Prog. Inorg. Chem.,* (ed. S. J. Lippard) *23,* 1, John Wiley and Sons, New York (1977).