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Metal–Phenoxyalkanoic Acid Interactions.
Part 6. Crystal and Molecular Structure of Tetraaquabis(2,4-dichlorophenoxyacetato)zinc(II)diaquabis(2,4-dichlorophenoxyacetato)zinc(II)

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The crystal structure of tetraaquabis(2,4-dichlorophenoxyacetato)zinc(II)diaquabis(2,4-dichlorophenoxyacetato)zinc(II) has been determined by direct methods from three-dimensional X-ray diffraction data and refined by least squares to a residual value of 0.068 for 2703 'observed' reflections. Crystals are orthorhombic, space group $Pna2_1$ *with 4 molecular 'dimers' in a cell of dimensions* a = *19.302(2),* b = *6.051(1),* c = *36.325(6) Å. The molecular units,* $\{[Zn(H_2O)_4(2,4\text{-}D)_2][Zn(H_2O)_2(2,4\text{-}D)_2]\}$ *consist of two discrete and stereochemically different complexes, one octahedral, the other tetrahedral about the zinc centres. The six-coordination about the first Zn comprises four oxygens from aqua ligands [Zn–O, 2.069(10)–2.147(9) Å] and two from the carboxyl groups of* trans-*related unidentate 2,4-dichlorophenoxyacetato ligands [Zn–O, 2.071(9), 2.121(9) Å]. The un-complexed carboxylate oxygens are tied into the complex unit by intramolecular hydrogen bonds to the water ligands (O···O, 2.66, 2.64 Å). The four-coordination about the second Zn comprises two aqua ligands [Zn–O, 2.003(10), 2.001(9) Å] and two unidentate carboxyl oxygens from 2,4-dichlorophenoxyacetato ligands [Zn–O, 1.915(10), 1.956(9) Å]. The two units are not formally bonded but have inter-molecular O···O associations ranging from 2.68 to 2.85 Å.*

Introduction

Phenoxyalkanoic acids interact with metal ions in aqueous media to form complexes which have been shown by X-ray diffraction methods to have diverse stereochemistries. The important commercial herbicide 2,4-dichlorophenoxyacetic acid, (2,4-D), is known to form three different complexes with copper(II). $[Cu_2(2,4\text{-}D)_4(H_2O)_2]\cdot 2H_2O$, a tetracarboxylate bridged dimer species was described in a previous article in this series [2]. Bonding for this complex and the dimeric species $[Cu_2(2,4,5\text{-}T)_4(py)_2]$ (2,4,5-T = 2,4,5-trichlorophenoxyacetato) is different from that found for the majority of other examples of phenoxy acid complexes of Cu^{II} which involve Cu^{II} in tetragonally distorted six-coordination with acid groups in various complexing modes [3]. Although bridged carboxylate complexes of Zn^{II} involving aqua ligands are known, *e.g.* zinc formate monohydrate [4] and zinc 2-ethoxybenzoate monohydrate [5] most zinc(II) complexes involve the acid in a discrete monomeric bonding with either tetrahedral or octahedral stereochemistries about zinc.

So far the only structures of zinc phenoxyalkanoates known are the isomorphous and isostructural zinc phenoxyacetate dihydrate and zinc 4-chlorophenoxyacetate dihydrate [3]. The asymmetric carboxylates complete a stereochemistry about Zn^{II} which is best described as skew-trapezoidal bipyramidal. The structure of the title compound was determined as part of a continuing investigation of the nature of bonding in metal–phenoxy herbicide complexes and to investigate the conformational changes in ligands resulting from complexation. This is possible because the structure of 2,4-D is known [6].

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[a] Part 5: Tetraaquabis(4-chloro-2-methylphenoxyacetato)magnesium(II) dihydrate, ref. [20].

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Experimental

Preparation of $[Zn(H_2O)_4(2,4\text{-}D)_2][Zn(H_2O)_2(2,4\text{-}D)_2]$

Using a previously described method [3], the title compound was prepared by reacting an aqueous ethanolic solution of 2,4-dichlorophenoxyacetic acid with excess zinc(II) carbonate. Large colourless needles were grown from this solution by slow cooling in a Dewar flask over a period of several days. Elemental analysis indicated a complex of formula $[Zn(2,4\text{-}D)_2(H_2O)_3]$ [Found: C, 34.2 H, 2.96; Cl, 24.4%. Calc. for the three-hydrate: C, 34.33 H, 2.86; Cl, 25.4%]. Although the % Cl suggested a four-hydrate, the density calculated for a three-hydrate (1.75 g cm^{-3}) was more consistent with the measured value (1.76 g cm^{-3}) than for the four-hydrate (1.81 g cm^{-3}).

Collection of X-ray Data and Structure Solution

A crystal measuring 0.27 × 0.37 × 0.15 mm was cleaved from a needle and mounted about the *b* (prism) axis on a Nonius CAD-4 four-circle diffractometer. Details regarding acquisition of crystal data and crystal cell parameters are given in Table I.

Data were corrected for Lorentz and monochromator polarization effects but not for absorption. Systematic absences were consistent with either space group *Pnam* or $Pna2_1$. Intensity statistics (mean $|E^2 - 1| = 0.928$) suggested the centrosymmetric one but the automatic Σ_2 sign expansion direct methods approach of SHELX 76 [7] failed to give a solution. Examination of the three-dimensional Patterson synthesis showed that the non-centrosymmetric space group was correct and that the zinc atoms occupied general positions rather than being confirmed to crystallographic mirror planes at $z = \frac{1}{4}, \frac{3}{4}$. The use of the tangent formula SHELX subsequently revealed the positions of the two zinc and eight chlorine atoms in an E-map. After three cycles of refinement and weighted difference-Fourier electron density synthesis all other non-hydrogen atoms were located and $R [= \Sigma||F_o - F_c||/|F_o|]$ was reduced from an initial value of 0.40 to a final 0.068 and an R_w [$= \Sigma w(||F_o - F_c||^2/\Sigma w|F_o|^2)^{1/2}$] of 0.075. A value of $w = 1/[\sigma^2(F_o) + 0.00049(F_o)^2]$ was used. Most hydrogens were located in difference-Fourier syntheses and were included in the refinement at fixed positions with their isotropic *U*s set invariant at 0.05 Å^2. The determination was based on a reduced data set of 2703 reflections with $I > 2.5\sigma(I)$ ($2\theta_{max} = 102°$). Anisotropic thermal parameters were used for zinc and chlorine atoms only. Four intense low-angle reflections (0, 0, 2; 0, 0, 4; 0, 0, 8; 0, 1, 9) were considered to be seriously affected by extinction and were removed before the final refinement cycle. A final difference-Fourier synthesis revealed no electron density greater than 0.38 e$Å^{-3}$. Scattering factors used were those of Cromer and Mann [8] (non-hydrogens) and Stewart *et al.* [9] (hydrogens). Zinc and chlorines were corrected for the effects of anomalous dispersion. Final positional parameters are given in Table II while interatomic distances and angles are listed in Table III. Lists of observed and calculated structure factor amplitudes have been deposited, and anisotropic thermal parameters for zinc and chlorines are given in Table IV.

TABLE I. Experimental Data for the X-ray Diffraction Study of $[Zn(H_2O)_4(2,4\text{-}D)_2][Zn(H_2O)_2(2,4\text{-}D)_2]$, $C_{32}H_{32}Cl_8O_{18}Zn_2$.

A. *Crystal Parameters*[a] at 25 (±) 1 °C

Crystal system: orthorhombic

Space group: $Pna2_1$ (C_{2v}^9 No. 33)

Equivalent positions: x, y, z; $\bar{x}, \bar{y}$, ½ + z; ½ – x, ½ + y, ½ + z;
½ + x, ½ – y, z

Cell dimensions: *a* = 19.302(2) Å
b = 6.051(1)
c = 36.325(6)

$V = 4242.7$ Å^3

$Z = 4$

Mol. wt. = 1118.4

ρ(calc.) = 1.75 g cm^{-3}

ρ(found) = 1.76 g cm^{-3}

F(000) = 2256

μ(Cu Kα) = 67.2 cm^{-1}

B. *Measurement of Data*

Diffractometer: Nonius CAD-4

Radiation: graphite monochromated Cu Kα (λ = 1.5418 Å)

2θ range: $2 \leqslant 2\theta \leqslant 140°$

Scanning mode: $\omega/2\theta$

Reflections collected: 4580 total; 4293 unique

Standards: (0, 1, 9), (4, 1, 5) collected every 48 reflections

Crystal size: 0.27 × 0.37 × 0.15 mm

Mean $|E^2 - 1|$: 0.928

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[a] Accurate cell parameters were obtained by least-squares refinement of angle data for 15 centred reflections using the Nonius system.

Discussion

The molecular units in the title compound consist of both octahedral $[Zn(H_2O)_4(2,4\text{-}D)_2]$ and tetrahedral $[Zn(H_2O)_2(2,4\text{-}D)_2]$ complexes (Figs. 1 and 2) linked only by hydrogen bonding associations with O···O distances ranging from 2.68 to 2.85 Å (Table V). The occurrence of both stereochemistries in the one crystal has been reported earlier for zinc(II)

TABLE II. Atomic Coordinates ($\times 10^4$) and Isotropic Temperature Factors ($Å^2$, $\times 10^3$) for $[Zn(H_2O)_4(2,4\text{-}D)_2][Zn(H_2O)_2(2,4\text{-}D)_2]$. A, B, C, D represent the four 2,4-dichlorophenoxyacetato ligands while the atom numbering scheme is that used for the un-complexed acid (2,4-D) [6].

	x/a	*y/b*	*z/c*	*U*		*x/a*	*y/b*	*z/c*	*U*
Zn(O)	4381(1)	2457(3)	309		H(O11)	5072	5593	416	
Ow(O1)	5109(4)	4868(15)	170(2)	26(2)	H(O12)	5075	5087	27	
Ow(O2)	3690(4)	3569(16)	−85(3)	33(2)	H(O21)	3550	2406	−222	
Ow(O3)	5034(4)	1335(15)	729(2)	25(3)	H(O22)	3756	5442	−67	
Ow(O4)	3645(4)	−37(14)	463(2)	25(2)	H(O31)	*			
O(11A)	4842(4)	236(15)	−49(2)	23(2)	H(O32)	*			
O(11B)	3936(4)	4714(15)	688(2)	24(2)	H(O41)	3793	−897	206	
Zn(T)	1878(1)	3261(3)	312(1)		H(O42)	3649	200	680	
Ow(T1)	1178(5)	5406(17)	117(3)	38(3)	H(T11)	1151	5597	374	
Ow(T2)	2589(4)	5356(16)	509(3)	29(3)	H(T12)	1374	6206	−143	
O(11C)	2354(4)	1888(16)	−90(3)	26(3)	H(T21)	2543	4664	703	
O(11D)	1399(4)	1889(16)	728(3)	28(3)	H(T22)	2611	5935	270	

	Ligand A				Ligand B			
Cl(2)	3879(2)	−7821(8)	−978(1)		4896(2)	12671(8)	1603(1)	
Cl(4)	5641(2)	−7559(9)	−2119(2)		3062(2)	12659(10)	2714(2)	
C(1)	4803(7)	−4520(24)	−1067(3)	18(4)	3957(7)	9469(22)	1706(4)	28(4)
C(2)	4542(7)	−6440(25)	−1219(4)	25(4)	4240(6)	11454(22)	1841(4)	33(4)
C(3)	4770(8)	−7461(31)	−1531(5)	50(5)	3988(5)	12399(19)	2172(3)	27(3)
C(4)	5296(6)	−6362(22)	−1720(4)	33(4)	3419(7)	11343(24)	2343(4)	36(4)
C(5)	5587(7)	−4341(28)	−1603(5)	55(5)	3139(6)	8415(23)	2216(4)	28(4)
C(6)	5310(7)	−3447(24)	−1274(4)	40(4)	3378(7)	8441(22)	1884(4)	31(3)
O(7)	4559(4)	−3823(17)	−742(3)	33(3)	4256(5)	8572(17)	1400(3)	30(3)
C(8)	4925(6)	−1999(20)	−579(3)	18(3)	3873(6)	6853(24)	1215(4)	32(4)
C(9)	4527(5)	−1188(19)	−246(3)	22(3)	4261(6)	6133(21)	888(3)	22(3)
O(10)	3921(5)	−1900(17)	−179(3)	34(3)	4849(4)	6825(15)	812(2)	25(3)
H(3)	4609	−9236	−1636		*			
H(5)	*				2827	8531	2403	
H(6)	*				3178	7016	1747	
H(81)	4870	−615	−799		3798	5505	1411	
H(82)	5400	−2421	−479		*			

	Ligand C				Ligand D			
Cl(2)	1231(2)	−6616(7)	−859(1)		2490(3)	−6630(10)	1472(2)	
Cl(4)	3023(3)	−7522(9)	−1992(2)		826(3)	−7275(10)	2650(2)	
C(1)	2280(6)	−3639(21)	−1000(4)	26(3)	1542(8)	−3585(27)	1644(5)	38(5)
C(2)	1953(6)	−5598(23)	−1101(3)	25(4)	1832(6)	−5564(24)	1756(4)	30(4)
C(3)	2134(6)	−6761(21)	−1397(3)	31(3)	1640(7)	−6712(25)	2090(4)	30(4)
C(4)	2680(6)	−6020(23)	−1620(4)	38(3)	1106(7)	−5679(26)	2286(4)	48(4)
C(5)	3020(6)	−3963(23)	−1528(4)	35(4)	765(7)	−3843(25)	2182(4)	45(4)
C(6)	2798(7)	−2893(21)	−1216(4)	34(3)	952(8)	−2714(27)	1859(5)	41(5)
O(7)	2024(4)	−2637(16)	−683(3)	44(4)	1759(4)	−2562(16)	1339(3)	30(3)
C(8)	2414(4)	−780(22)	−552(4)	27(3)	1357(5)	−690(21)	1199(3)	23(3)
C(9)	2041(6)	200(20)	−230(3)	20(3)	1699(7)	229(24)	874(4)	28(4)
O(10)	1479(4)	−461(13)	−105(2)	30(2)	2263(4)	−512(15)	746(2)	30(2)
H(3)	*				*			
H(5)	*				410	−2881	2387	
H(6)	*				685	−1286	1714	
H(81)	2418	413	−723		1326	470	1373	
H(82)	*				*			

*Not located.

TABLE III. Bond Distances (Å) and Angles (deg) (estimated standard deviations in parentheses) Compared with 2,4-D [6].

a. *Distances*

Zn(O)–Ow(O1)	2.088(10)	Zn(T)–Ow(T1)	2.003(10)
Zn(O)–Ow(O2)	2.069(10)	Zn(T)–Ow(T2)	2.001(9)
Zn(O)–Ow(O3)	2.092(9)	Zn(T)–O(11C)	1.915(10)
Zn(O)–Ow(O4)	2.147(9)	Zn(T)–O(11D)	1.956(9)
Zn(O)–O(11A)	2.071(9)		
Zn(O)–O(11B)	2.121(9)		

	Ligand A	Ligand B	Ligand C	Ligand D	2,4-D
C(1)–C(2)	1.381(20)	1.408(19)	1.392(18)	1.383(19)	1.390(6)
C(2)–C(3)	1.364(23)	1.417(18)	1.332(18)	1.446(19)	1.384(6)
C(2)–Cl(2)	1.761(14)	1.701(14)	1.758(15)	1.759(13)	1.741(4)
C(3)–C(4)	1.394(22)	1.414(17)	1.403(17)	1.400(20)	1.395(6)
C(4)–C(5)	1.411(21)	1.366(19)	1.446(19)	1.345(21)	1.364(7)
C(4)–Cl(4)	1.752(14)	1.710(15)	1.758(15)	1.724(16)	1.741(4)
C(5)–C(6)	1.417(20)	1.419(18)	1.374(19)	1.405(22)	1.413(7)
C(6)–C(1)	1.395(22)	1.433(18)	1.349(18)	1.478(22)	1.397(7)
C(1)–O(7)	1.339(17)	1.365(16)	1.392(15)	1.336(19)	1.365(5)
O(7)–C(8)	1.438(15)	1.442(17)	1.434(16)	1.464(15)	1.423(5)
C(8)–C(9)	1.515(15)	1.470(19)	1.496(17)	1.462(20)	1.520(6)
C(9)–O(10)	1.270(14)	1.241(14)	1.242(14)	1.266(20)	1.217(6)
C(9)–O(11)	1.274(14)	1.288(15)	1.291(15)	1.275(21)	1.304(5)

b. *Angles*

O(11A)–Zn(O)–O(11B)	178.1(4)	O(11C)–Zn(T)–O(11D)	129.2(4)
O(11A)–Zn(O)–Ow(O1)	90.7(4)	O(11C)–Zn(T)–Ow(T1)	109.6(4)
O(11A)–Zn(O)–Ow(O2)	93.1(4)	O(11C)–Zn(T)–Ow(T2)	102.6(4)
O(11A)–Zn(O)–Ow(O3)	89.3(4)	O(11D)–Zn(T)–Ow(T1)	103.3(4)
O(11A)–Zn(O)–Ow(O4)	89.5(4)	O(11D)–Zn(T)–Ow(T2)	108.5(4)
O(11B)–Zn(O)–Ow(O1)	88.8(4)	Ow(T1)–Zn(T)–Ow(T2)	100.3(4)
O(11B)–Zn(O)–Ow(O2)	88.8(4)	Zn(T)–O(11C)–C(9C)	114.8(4)
O(11B)–Zn(O)–Ow(O3)	88.8(4)	Zn(T)–O(11D)–C(9D)	116.2(4)
O(11B)–Zn(O)–Ow(O4)	90.9(4)		
Ow(O1)–Zn(O)–Ow(O2)	92.3(4)		
Ow(O1)–Zn(O)–Ow(O3)	89.9(4)		
Ow(O1)–Zn(O)–Ow(O4)	178.7(4)		
Ow(O2)–Zn(O)–Ow(O3)	176.8(4)		
Ow(O2)–Zn(O)–Ow(O4)	89.0(4)		
Ow(O3)–Zn(O)–Ow(O4)	88.9(4)		
Zn(O)–O(11A)–C(9A)	125.9(4)		
Zn(O)–O(11B)–C(9B)	126.7(4)		

	Ligand A	Ligand B	Ligand C	Ligand D	2,4-D
C(2)–C(1)–C(6)	115.6(12)	121.1(12)	117.9(12)	117.7(13)	119.1(2)
C(2)–C(1)–O(7)	119.3(12)	117.3(12)	115.3(12)	121.2(13)	116.2(3)
C(6)–C(1)–O(7)	125.1(12)	121.6(12)	126.8(13)	121.0(13)	124.7(3)
C(1)–C(2)–C(3)	126.6(14)	120.4(11)	122.9(12)	124.0(12)	122.2(2)
C(1)–C(2)–Cl(2)	117.3(11)	118.8(10)	121.7(10)	115.9(11)	118.9(2)
C(3)–C(2)–Cl(2)	115.6(12)	120.8(10)	115.2(11)	120.1(12)	118.8(2)
C(2)–C(3)–C(4)	115.4(15)	117.2(11)	119.6(12)	113.6(13)	117.3(2)
C(3)–C(4)–C(5)	123.7(14)	123.0(12)	118.9(12)	125.9(14)	122.7(2)
C(3)–C(4)–Cl(4)	119.1(11)	116.7(10)	124.2(11)	111.8(11)	117.6(2)

TABLE III. (*Continued*)

C(5)–C(4)–Cl(4)	117.1(11)	120.3(10)	116.9(11)	121.6(12)	119.6(2)
C(4)–C(5)–C(6)	115.6(18)	120.9(12)	117.1(12)	120.7(14)	119.1(2)
C(5)–C(6)–C(1)	122.8(12)	117.2(12)	123.6(12)	117.8(14)	119.6(2)
C(1)–O(7)–C(8)	115.6(10)	116.7(10)	115.4(11)	118.7(10)	118.8(4)
O(7)–C(8)–C(9)	109.2(11)	109.2(10)	108.5(10)	109.6(11)	111.1(3)
C(8)–C(9)–O(10)	120.7(11)	123.1(11)	125.3(11)	123.4(11)	123.2(3)
C(8)–C(9)–O(11)	115.2(10)	113.9(10)	113.5(10)	115.5(12)	112.2(2)
O(10)–C(9)–O(11)	124.1(11)	123.0(10)	121.3(11)	121.1(11)	124.5(2)

TABLE IV. Anisotropic Thermal Parameters (Å^2, $\times 10^3$) for Zn and Cl Atoms.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(O)	10(1)	22(1)	25(1)	2(1)	3(1)	1(1)
Zn(T)	12(1)	26(1)	28(1)	5(1)	−1(1)	0(1)
Cl(2A)	42(2)	41(3)	42(3)	−3(2)	0(2)	18(2)
Cl(2B)	37(3)	45(3)	55(4)	−9(2)	2(3)	−20(2)
Cl(2C)	17(2)	38(3)	60(3)	4(2)	−1(2)	4(2)
Cl(2D)	29(3)	35(3)	52(3)	−2(3)	−11(2)	−8(2)
Cl(4A)	58(4)	85(5)	39(4)	31(3)	−12(3)	−1(3)
Cl(4B)	62(4)	108(5)	49(4)	−40(3)	7(3)	−3(3)
Cl(4C)	70(4)	74(4)	40(4)	−27(3)	6(3)	−14(3)
Cl(4D)	68(3)	92(4)	47(4)	33(3)	−4(4)	−9(3)

TABLE V. Hydrogen Bonding Interactions less than 3 Å; primed atoms are symmetry generated from the listed atomic coordinates; *intra* = intramolecular; *inter* = intermolecular; *o* = octahedral; *t* = tetrahedral.

Contact	Distance (Å)	Contact type
Ow(O1)–O(10B)	2.663	*intra (o–o)*
O(10C)	2.849	*inter (o–t)*
Ow(O2)–O(11C)	2.772	*inter (o–t)*
O(10A′)	2.799	*inter (o–o′)*
Ow(O3)–O(11D′)	2.845	*inter (o–t′)*
O(10B′)	2.769	*inter (o–o′)*
Ow(O4)–O(10A)	2.644	*intra (o–o)*
O(10D)	2.873	*inter (o–t)*
Ow(T1)–O(11A′)	2.677	*inter (t–o′)*
O(10C′)	2.691	*inter (t–t′)*
Ow(T2)–O(11B)	2.708	*inter (t–o)*
O(11D′)	2.718	*inter (t–t′)*

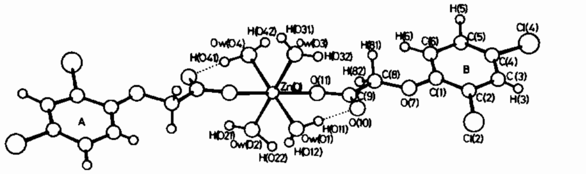

Fig. 1.

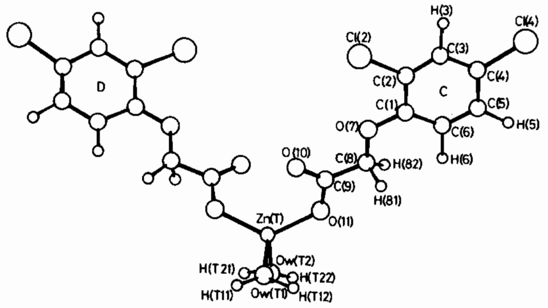

Fig. 2.

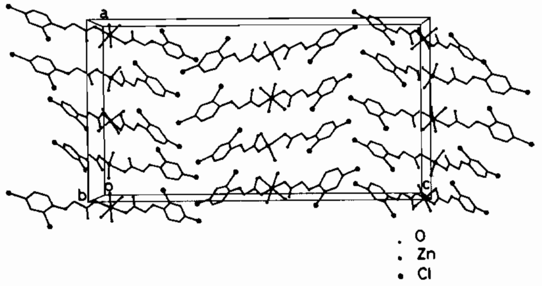

Fig. 3.

TABLE VI. Torsion Angles in the 2,4-Dichlorophenoxyacetato Ligands Compared with the Un-complexed Free Acid (2,4-D) [6].

	Ligand A	Ligand B	Ligand C	Ligand D	2,4-D
C(2)–C(1)–O(7)–C(8)	+171.5	−166.1	+172.4	+169.5	+179.1
C(1)–O(7)–C(8)–C(9)	+171.5	+178.4	+175.6	+177.8	+80.4
O(7)–C(8)–C(9)–O(11)	+171.2	−175.0	+179.7	−179.5	−173.1

complexes. Examples are Hopeite [$Zn_3(PO_4)_2 \cdot 4H_2O$] [10], $Zn_2Mo_3O_8$ [11], $Zn_4SiO_7(OH)_2 \cdot H_2O$ [12], $Zn(PO_4)_2 \cdot 4H_2O$ [13], $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ [14], $Zn_3(BO_3)_2$ [15], $ZnCO_3 \cdot 2.5H_2O$ [16], Zn(triethanolamine)$Cl_2 \cdot H_2O$ [17], Zn(EDTA)$\cdot 6H_2O$ [18]. However for most other examples, there is interlinking bonding via the anionic group resulting in bridged polymeric structures. In the case of the title compound, the 2,4-dichlorophenoxyacetato groups form discrete layers and pack into the structure in an almost parallel manner in the approximate *a* direction with ribbons of [$Zn(H_2O)_n$] units and phenoxy groups alternating along [001]. (Fig. 3).

[$Zn(H_2O)_4(2,4\text{-}D)_2$] — Octahedral Zn(II)

The coordination sphere about Zn(O) consists of four oxygens from water ligands [Zn–O, 2.069(10)–2.147(9) Å, mean 2.098 Å] and two from unidentate *trans*-related 2,4-D anions [Zn–O, 2.071(9), 2.121(9) Å] (Fig. 1). The overall mean (2.098 Å) compares closely with 2.099 Å for the octahedral environment in Hopeite and other examples in ref. [10]. The molecular symmetry approximates $\bar{1}$ with a slightly distorted octahedral stereochemistry analogous to the phenoxyalkanoic acid complexes: (a) tetraaquabis(phenoxyacetato)nickel(II) [19]; (b) the tetraaquabis(2,4,5-trichlorophenoxyacetato)manganese(II) complex in the [$Mn(H_2O)_4(2,4,5\text{-}T)_2$]$\cdot$2(2,4,5-TH) adduct [1]; (c) tetraaquabis(4-chloro-2-methylphenoxyacetato)magnesium(II) dihydrate [20]. The unidentate complexing mode is further stabilized by the presence of intra-molecular hydrogen bonding between the un-complexed carboxyl oxygens [O(10B), O(10A)] and the complexed aqua ligands [Ow(O1), 2.663; Ow(O4), 2.644 Å with OH···O angles of 172 and 169° respectively. This results in the formation of an open six-membered ring. All aqua ligands are involved in intermolecular hydrogen bonding links with either carboxyl oxygens of adjacent octahedral units (2) or with adjacent tetrahedral units (4) (Table V).

[$Zn(H_2O)_2(2,4\text{-}D)_2$] — Tetrahedral Zn(II)

The four-coordinate unit has two aqua ligands, [Zn–O, 2.003(10), 2.001(9) Å] and two unidentate carboxylate ligands [Zn–O, 1.915(10), 1.956(9) Å] with a distorted tetrahedral stereochemistry and approximate two-fold rotational symmetry (Fig. 2). The observed contraction in the bond indicates a significant bond strengthening compared to the analogous diaquabis(phenoxyacetato)zinc(II) complex [Zn–OH_2, 1.994(1) Å, Zn–O(carboxyl), 2.118(1) Å [3]. These lengths are comparable to the Zn–O distances in tetrahedral environments for previously mentioned examples [10–18] (1.953–1.978 Å) and in the ZnO structure (1.967, 1.976 Å) [21]. Most angles about Zn(T) are normal for a tetrahedron, except for O(11C)–Zn(T)–O(11D) [129.2(4)°] which could due to repulsion between the two separate 2,4-D ligands (Fig. 2). In the case of the phenoxyacetic acid analogue [3] and zinc *o*-chlorobenzoate monohydrate [22], the bonding to the acid group is via unsymmetrical bidentate carboxylate oxygens [Zn–O, 2.118, 2.337 Å and 2.054, 2.314 Å respectively). The first example is best described in terms of a skew-trapezoidal bipyramid. In both compounds the O–Zn–O angles are much larger than normal (142.4, 148.0°) because of the smaller degree of asymmetry compared with those of the present example (Zn–O; 2.873, 2.830 Å). The determining factor for asymmetry is probably the repulsion energy involved because of the larger steric influence of the 2,4-D groups compared with the phenoxy or *o*-chlorobenzoate groups. Furthermore repulsion energy calculations [23] show that as the metal–unidentate ligand bond length decreases relative to the metal–bidentate ligand bond length in the six-coordinate [metal(bidentate)$_2$(unidentate)$_2$] system, the distortion to the skew trapezoidal bipyramidal stereochemistry is at larger values of 'normalized bite'. This may be the reason for the change from octahedral to tetrahedral stereochemistries with little energy difference between the two forms.

Intra-ligand bond distances and angles for all independent ligands are similar and show the same features as found in the un-complexed 2,4-D acid molecule [6]. The trends observed within the phenoxyalkanoic acids [24, 25] include: (a) distortion of the exo-C(1) bond angles away from C(6); (b) distortion of the C(8)–C(9)–O(11) angles [113.9–115.5(10)°] and C(8)–C(9)–O(10) angles [120.7–125.3(10)°]. This allows identification of the two oxygens as having either 'hydroxyl' [O(11)] or 'carbonyl' [O(10)] origin. This discrete angle distortion has been observed without exception among complexes of phenoxyalkanoic acids [1–3]. In both the octahedral and the tetrahedral complexes, bonding is via the 'hydroxyl' oxygen and the *syn–syn* ('carbonyl') conformation of 2,4-D and of all known phenoxyacetic acids is retained. This places the O(ether) [O(7)] and O('carbonyl') [O(10)] oxygens at interactive distances of 2.656, 2.644, 2.692, 2.669 Å (ligands A to D respectively), which are closely comparable with the range and mean of 2.605 Å [2,4,5-T] to 2.775 Å [2-(*p*-chlorophenoxy)propionic acid], mean 2.711 Å, 17 examples of phenoxyalkanoic acids [25].

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