Inorganica Chimica Acta, *100* (1985) 267–273

Metal–Phenoxyalkanoic Acid Interactions.
Part 15.* The Crystal Structures of Diaquabis(phenoxyacetato)cadmium(II) and *Catena*-μ-[aquabis(phenoxyacetato-*O*)lead(II)-bis(phenoxyacetato)lead(II)]

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Received August 13, 1984

Abstract

The crystal structures of the cadmium(II) and lead(II) complexes of phenoxyacetic acid (PAH) have been determined by single crystal X-ray diffraction techniques. The cadmium complex, $[Cd(PA)_2(H_2O)_2]$ (1), space group $C2$, with $Z = 2$ in a cell of dimensions, a = 11.801(2), b = 5.484(1), c = 13.431(3) Å, β = 100.87(2)°, possesses a distorted trapezoidal bipyramidal coordination around the metal atom, involving two water oxygens [2.210(5) Å] and four carboxyl oxygens from two symmetrical bidentate phenoxyacetate ligands [2.363(4), 2.365(4) Å] with Cd lying on the crystallographic two-fold axis. The lead complex, $[Pb_2(PA)_4(H_2O)]_n$ (2) is triclinic, space group $P\bar{1}$, $Z = 2$, with a cell of dimensions, a = 10.135(4), b = 10.675(3), c = 19.285(9) Å, α = 114.66(3), β = 91.94(3) and γ = 114.99(3)°. (2) is a two-dimensional polymer with a repeating dimer sub-unit. The first lead [Pb(1)] has an irregular MO_8 coordination [2.34–2.96(2) Å: mean, 2.63(2) Å] involving the water molecule, two oxygens from an asymmetric bidentate carboxylate group, two from a bidentate chelate [O(ether), O(carboxylate)] group and three from bridging oxygens, one of which also provides a polymer link to another symmetry generated lead. The second lead [Pb(2)] is irregular seven-coordinate [Pb–O, 2.48–2.73(2) Å: mean, 2.61(2) Å] with three bonds from the bridging groups, two from an unsymmetrical bidentate carboxylate (*O*, *O*′) group and one from a second carboxyl group which also bridges two Pb(2) centres in the polymer.

Introduction

The structural chemistry of a number of metal–phenoxyalkanoic acid complexes has been reported in previous papers in this series. These include complexes with the following metals: Cu^{II} [1, 3, 8, 13]; Zn^{II} [1, 6]; Mn^{II} [2, 4, 7, 9, 10]; Ni^{II} [10, 12]; Mg [2, 5, 7] and K [11].

This work has now been extended to include Cd^{II} and Pb^{II}. The structures of the phenoxyacetate complexes of cadmium(II) $[Cd(PA)_2(H_2O)_2]$ (1) and lead(II) $[Pb_2(PA)_4(H_2O)]_n$ (2) were determined to assess the role of the phenoxyacetate oxygens in heavy metal coordination. The cadmium complex of a related acid, (phenylthio)acetic acid (PTAH), {*catena* - aquabis [(phenylthio)acetato] cadmium(II)} [14], has an octahedral MO_5S coordination sphere consisting of one water [Cd–O, 2.294(10) Å], an oxygen and a sulphur from one (phenylthio)acetate (PTA) ligand [Cd–O, 2.335(10) Å; Cd–S, 2.738(5) Å] and an oxygen from the second PTA ligand [Cd–O, 2.276(10) Å]. The second carboxyl oxygen from each PTA ligand completes the fifth and sixth coordination sites [Cd–O, 2.263(12), 2.254(10) Å] and bridges adjacent complex centres giving a polymeric structure. In a corresponding zinc complex $[Zn(PTA)_2(H_2O)_2]$ [14], there is a distorted octahedral coordination around the metal atom, involving four oxygens from two symmetrical bidentate PTA carboxyl groups [Zn–O, 2.176(4), 2.204(3) Å] and two from *cis* related waters [Zn–O, 2.002(4) Å].

Experimental

Preparation of $[Cd(PA)_2(H_2O)_2]$ (1) and $[Pb_2(PA)_4(H_2O)]_n$ (2)

The complexes were prepared by reacting phenoxyacetic acid (PAH), in aqueous ethanol with a

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*Part 14: ref. [14].

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0020-1693/85/$3.30

suspension of excess metal carbonate (in aqueous ethanol), and digesting for one hour at 70–90 °C. The unreacted carbonate was filtered off, and the filtrate, on cooling, yielded crystals which were recrystallised as easily deformed flat needles (1) or prisms (2) from ethanol.

Crystal Data, X-ray Data Collection and Structure Refinement

Table I details unit cell parameters, data acquisition, structure solution and refinement for compounds (1) and (2). Data were processed using a profile fitting procedure [15], and corrected for absorption. Structures were solved and refined using the SHELX-76 program set [16]. In the case of (1), the structure was determined using the heavy atom method while for (2), the two lead atoms were located using the multisolution Σ_2 sign expansion direct methods procedure of SHELX, and confirmed by a Patterson synthesis. The remaining non-hydrogen atoms were located using weighted difference-Fouriers. Blocked-matrix least-squares refinement was used, with all non-hydrogen atoms anisotropic for (1) but only the atoms of the coordination sphere anisotropic in (2). The residuals are defined as follows:

$$R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$$

and

$$R_w = [(\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}]$$

Hydrogens for both compounds were located from difference-Fourier syntheses and included in the refinements at fixed positions with their isotropic

TABLE I. Experimental Data.

	$[Cd(PA)_2(H_2O)_2]$	$[Pb_2(PA)_4(H_2O)]_n$
(a) Crystal Parameters		
Formula	$C_{16}H_{18}CdO_8$	$C_{32}H_{30}O_{13}Pb_2$
M_r	450.7	1037.0
Space group	$C2$	$P\bar{1}$
a (Å)	11.801(2)	10.135(4)
b (Å)	5.484(1)	10.675(3)
c (Å)	13.431(3)	19.285(9)
α (°)	–	114.66(3)
β (°)	100.87(2)	91.94(3)
γ (°)	–	114.99(3)
V (Å^3)	853.6(3)	1661.8(9)
Z	2	2
ρ(calc.) (g cm^{-3})	1.752	2.072
ρ(found) (g cm^{-3})	1.76	2.10
F(000)	452	980
μ(MoKα) (cm^{-1})	13.2	100.2
(b) Measurement of Data		
Diffractometer	Nicolet R3m	Nicolet R3m
Radiation	MoKα	MoKα
λ (Å)	0.7107	0.7107
Reflections measured:		
2θ maximum (°)	52	54
Scanning mode	$2\theta/\omega$	$2\theta/\omega$
Reflections collected:		
Total	935	6005
Observed	904	2451 (limited data set used)
$I > n\sigma(I)$ where n =	2.5	3.0
Corrections applied, transmission factors	0.565–0.664	0.231–0.939
Crystal size (mm)	0.40 × 0.24 × 0.04	0.40 × 0.38 × 0.18
R	0.025	0.070
R_w	0.027	0.077
Maximum background in final difference map (e Å^{-3})	0.50	0.40
Weighting scheme:		
$A/(\sigma^2F_o + BF_o^2)$ A	0.67	2.3
B	1 × 10^{-4}	2 × 10^{-4}
Reflections suffering from extinction	001, 003	−220, 2−33

U's set invariant at 0.05 Å^2. Neutral atom scattering factors were used [17], and corrected where appropriate for anomalous dispersion [17]. Final atomic parameters are given in Table II, while anisotropic thermal parameters and observed and calculated structure factors are available from the authors. Bond distances and angles are given in Tables III and IV.

TABLE 11. Atomic Coordinates (×10^4).

Atom	*x*/*a*	*y*/*b*	*z*/*c*
(a) [Cd(phenoxy)$_2$(H$_2$O)$_2$] (1)			
Cd	2253(5)	8417(12)	2847(4)
C(1)	1682(4)	9944(38)	3375(4)
C(2)	2252(6)	11723(14)	4023(5)
C(3)	3419(8)	11932(16)	4139(5)
C(4)	4052(5)	10419(21)	3601(5)
C(5)	3475(5)	8645(13)	2954(5)
C(6)	1682	9944	3375
O(7)	1623(3)	6748(9)	2229(3)
C(8)	2210(4)	5083(32)	1718(3)
C(9)	1425(4)	3170(11)	1167(4)
O(10)	372(3)	3109(8)	1237(3)
O(11)	1842(3)	1656(8)	645(3)
Ow	−857(3)	−2756(9)	803(4)
(b) [Pb$_2$(PA)$_4$(H$_2$O)]$_n$ (2)			
Molecule A			
Pb	4046(1)	−4310(1)	−635(1)
Ow	8352(18)	−2986(19)	791(14)
C(1)	1313(26)	−3532(25)	2374(21)
C(2)	449(45)	−3364(43)	2858(30)
C(3)	1428(46)	−2336(44)	3711(30)
C(4)	2732(47)	−1741(43)	3939(29)
C(5)	3481(51)	−1878(50)	3431(33)
C(6)	2825(33)	−2889(33)	2610(24)
O(7)	386(21)	−4576(21)	1584(15)
C(8)	1050(25)	−4735(25)	962(20)
C(9)	1622(21)	−3379(22)	831(18)
O(10)	1370(18)	−2231(18)	1204(14)
O(11)	2493(17)	−3282(17)	376(13)
Molecule B			
Pb	3740(1)	9708(1)	886(1)
Ow	–	–	–
C(1)	6849(28)	7458(27)	2753(23)
C(2)	6470(34)	6214(32)	2931(26)
C(3)	7049(43)	6456(42)	3685(32)
C(4)	7841(47)	7869(49)	4311(31)
C(5)	8209(40)	9144(41)	4189(31)
C(6)	7773(35)	8942(40)	3423(26)
O(7)	6310(18)	7092(18)	2069(14)
C(8)	6619(24)	8370(24)	1893(19)
C(9)	5802(22)	7663(33)	1040(19)
O(10)	5163(15)	6231(16)	610(12)
O(11)	5752(17)	8606(16)	787(13)
Molecule C			
C(1)	2710(25)	−2531(25)	−2756(23)
C(2)	3954(31)	−2251(30)	−3165(26)
C(3)	3703(14)	−2575(40)	−4015(32)
C(4)	2362(39)	−3000(37)	−4324(26)
C(5)	1172(33)	−3251(33)	−3982(28)
C(6)	1350(29)	−2917(29)	−3164(25)
O(7)	3007(17)	−2222(17)	−2029(16)
C(8)	1891(21)	−2128(21)	−1562(18)
C(9)	2585(23)	−1538(23)	−748(19)
O(10)	1819(17)	−1157(18)	−280(13)
O(11)	3788(15)	−1449(17)	−533(13)
Molecule D			
C(1)	1844(25)	1822(27)	2295(21)
C(2)	1631(31)	906(32)	2700(25)
C(3)	1918(59)	1626(64)	3313(39)
C(4)	2507(58)	2967(62)	3836(36)
C(5)	2874(36)	4008(38)	3518(27)
C(6)	2463(32)	3387(33)	2780(24)
O(7)	1338(19)	981(20)	1477(15)
C(8)	1425(25)	1822(25)	1046(20)
C(9)	3006(22)	2600(22)	954(18)
O(10)	4044(16)	2433(18)	1219(14)
O(11)	3202(18)	3355(19)	563(14)

Discussion

[Cd(PA)$_2$(H$_2$O)$_2$] (1)

Complex (**1**) is isostructural and isomorphous with the corresponding Zn^{II} complex (Fig. 1) [comparative cell data, $a = 11.625(3)$, $b = 5.221(1)$, $c = 13.767(4)$ Å, $\beta = 101.05(5)°$, $Z = 2$, space group, *C*2]. Both complexes possess distorted trapezoidal bipyramidal stereochemistries [18], involving two water oxygens [2.210(5) Å (Cd^{II}); 1.994(1) Å (Zn^{II})] and four carboxyl oxygens from two bidentate and essentially planar phenoxyacetate ligands [2.363(4), 2.365(4) Å (Cd^{II}) and 2.118(1), 2.337(1) Å (Zn^{II})]. The metal atom in each case lies on the crystallographic two-fold rotational axis. The major differences between the two lie in the M–Ow distances and in the change from the asymmetric bidentate mode in the Zn^{II} complex [14] to a symmetric bidentate one in (**1**). A similar symmetrical bidentate system is also found in the (phenylthio)acetato complex, [Zn(PTA)$_2$(H$_2$O)$_2$] [Zn–O, 2.176, 2.204 Å] (distorted octahedral) [14]. The extreme case is reached in [Zn(2,4-D)$_2$(H$_2$O)$_2$]. [Zn(2,4-D)$_2$(H$_2$O)$_4$] [6] where a unidentate complexing mode is found, involving both octahedral and tetrahedral coordination centres. The analogy between the Zn^{II} and Cd^{II} phenoxyacetate complexes does not extend to the Cd^{II}–(phenylthio)acetate complex, which, as previously described,

TABLE III. Bond Distances (Å) and Angles (°) about the Coordination Sphere for (**1**) (compared with [Zn(PA)$_2$(H$_2$O)$_2$] [1]) and for (**2**).

(a) Distances

	(1)	[Zn(PA)$_2$(H$_2$O)$_2$]
M–Ow	2.210(5)	1.994(1)
M–O(10)	2.363(4)	2.118(1)
M–O(11)	2.365(4)	2.337(1)

	(2)		(2)
Pb(1)–O(11)A^a	2.71(2)	Pb(2)–O(10)A	2.72(2)
Pb(1)–O(7)B	2.96(2)	Pb(2)–O(11)A	2.58(2)
Pb(1)–O(10)B	2.51(2)	Pb(2)–O(11)B	2.73(2)
Pb(1)–O(10)B^b	2.34(2)	Pb(2)–O(10)C	2.48(2)
Pb(1)–O(11)B^a	2.87(2)	Pb(2)–O(11)C	2.73(2)
Pb(1)–O(10)D	2.79(2)	Pb(2)–O(11)C^a	2.50(2)
Pb(1)–O(11)D	2.51(2)	Pb(2)–O(10)D	2.58(2)
Pb(1)–Ow	2.76(2)		

(b) Angles

	(1)	[Zn(PA)$_2$(H$_2$O)$_2$]
Ow–M–O(10)	101.1(2)	99.2(1)
Ow–M–O(10)^c	142.7(2)	142.5(1)
Ow–M–Ow^c	93.6(2)	93.9(1)
O(10)–M–O(10)^c	87.6(2)	91.4(1)
O(10)–M–O(11)	55.2(1)	58.6(1)
O(10)–M–O(11)^c	90.9(1)	84.7(1)
O(11)–M–Ow	123.9(1)	122.1(1)

	(2)		(2)
O(11)A^a–Pb(1)–O(7)B	142.0(6)	O(10)A–Pb(2)–O(11)A	48.8(6)
O(11)A^a–Pb(1)–O(10)B	121.4(6)	O(10)A–Pb(2)–O(11)B	104.9(7)
O(11)A^a–Pb(1)–O(10)B^b	72.8(7)	O(10)A–Pb(2)–O(10)C	83.9(7)
O(11)A^a–Pb(1)–O(11)B^a	62.8(6)	O(10)A–Pb(2)–O(11)C	174.5(6)
O(11)A^a–Pb(1)–O(10)D	121.1(6)	O(10)A–Pb(2)–O(11)C^a	113.6(6)
O(11)A^a–Pb(1)–O(11)D	133.5(7)	O(10)A–Pb(2)–O(10)D	118.0(6)
O(11)A^a–Pb(1)–Ow	75.2(7)	O(11)A–Pb(2)–O(11)B	66.4(5)
O(7)B–Pb(1)–O(10)B	56.3(7)	O(11)A–Pb(2)–O(10)C	81.3(7)
O(7)B–Pb(1)–O(10)B^b	120.1(7)	O(11)A–Pb(2)–O(11)C	126.2(6)
O(7)B–Pb(1)–O(11)B^a	154.0(7)	O(11)A–Pb(2)–O(11)C^a	74.6(6)
O(7)B–Pb(1)–O(10)D	88.0(6)	O(11)A–Pb(2)–O(10)D	160.3(5)
O(7)B–Pb(1)–O(11)D	83.4(5)	O(11)B–Pb(2)–O(10)C	122.8(6)
O(7)B–Pb(1)–Ow	69.6(6)	O(11)B–Pb(2)–O(11)C	69.8(6)
O(10)B–Pb(1)–O(10)B^b	65.8(6)	O(11)B–Pb(2)–O(11)C^a	73.7(5)
O(10)B–Pb(1)–O(11)B^a	107.9(6)	O(11)B–Pb(2)–O(10)D	132.6(4)
O(10)B–Pb(1)–O(10)D	111.7(6)	O(10)C–Pb(2)–O(11)C	97.9(7)
O(10)B–Pb(1)–O(11)D	68.5(6)	O(10)C–Pb(2)–O(11)C^a	52.1(7)
O(10)B–Pb(1)–Ow	67.7(6)	O(10)C–Pb(2)–O(10)D	82.6(6)
O(10)B^b–Pb(1)–O(11)B^a	49.0(6)	O(11)C–Pb(2)–O(11)C^a	64.2(6)
O(10)B^b–Pb(1)–O(10)D	113.8(6)	O(11)C–Pb(2)–O(10)D	67.4(6)
O(10)B^b–Pb(1)–O(11)D	74.0(6)	O(11)C^a–Pb(2)–O(10)D	104.0(6)
O(10)B^b–Pb(1)–Ow	90.0(6)		
O(11)B^a–Pb(1)–O(10)D	78.0(7)		
O(11)B^a–Pb(1)–O(11)D	70.9(7)		
O(11)B^a–Pb(1)–Ow	127.1(7)		
O(10)D–Pb(1)–O(11)D	49.4(8)		
O(10)D–Pb(1)–Ow	153.7(7)		
O(11)D–Pb(1)–Ow	136.0(7)		

$^a1-x, -y, -z$. $^b1-x, 1-y, -z$. $^c-x, y, -z$.

TABLE IV. Comparative Intraligand Bond Distances and Angles.

	(1)	$[Zn(PA)_2(H_2O)_2]$	(2)			
			A	B	C	D
(a) Distances						
C(1)–C(2)	1.356(15)	1.393(4)	1.31(4)	1.41(4)	1.50(4)	1.44(4)
C(2)–C(3)	1.393(17)	1.381(4)	1.54(4)	1.42(4)	1.52(4)	1.05(5)
C(3)–C(4)	1.361(12)	1.385(4)	1.17(5)	1.33(5)	1.27(5)	1.21(5)
C(4)–C(5)	1.404(12)	1.377(4)	1.26(5)	1.38(4)	1.38(4)	1.41(5)
C(5)–C(6)	1.394(11)	1.391(4)	1.42(4)	1.42(4)	1.45(4)	1.26(4)
C(6)–C(1)	1.427(8)	1.389(4)	1.35(4)	1.42(4)	1.37(4)	1.35(5)
C(1)–O(7)	1.359(7)	1.367(3)	1.43(4)	1.24(4)	1.29(4)	1.39(4)
O(7)–C(8)	1.401(13)	1.430(3)	1.38(4)	1.45(4)	1.48(4)	1.44(4)
C(8)–C(9)	1.499(6)	1.499(4)	1.45(4)	1.52(4)	1.44(3)	1.52(4)
C(9)–O(10)	1.264(6)	1.266(3)	1.28(4)	1.23(4)	1.26(3)	1.26(4)
C(9)–O(11)	1.246(7)	1.260(3)	1.27(4)	1.31(4)	1.23(3)	1.28(4)
(b) Angles						
C(2)–C(1)–O(7)	117.8(6)	115.3(2)	109(2)	116(2)	120(2)	116(2)
C(6)–C(1)–O(7)	123.1(6)	124.4(2)	127(2)	132(2)	124(2)	130(2)
C(2)–C(1)–C(6)	119.1(7)	120.4(3)	124(2)	112(2)	116(2)	114(2)
C(1)–C(2)–C(3)	122.0(6)	119.4(3)	109(2)	123(2)	123(2)	111(2)
C(2)–C(3)–C(4)	119.3(7)	121.0(3)	129(2)	123(2)	113(2)	145(3)
C(3)–C(4)–C(5)	121.1(7)	119.1(3)	117(3)	117(3)	127(3)	110(3)
C(4)–C(5)–C(6)	119.2(6)	121.2(3)	124(2)	121(2)	122(2)	116(3)
C(5)–C(6)–C(1)	119.3(6)	118.9(3)	116(2)	124(2)	118(2)	123(2)
C(1)–O(7)–C(8)	118.3(5)	115.6(2)	119(2)	117(2)	109(2)	118(2)
O(7)–C(8)–C(9)	112.4(4)	110.9(2)	114(2)	108(2)	114(2)	111(2)
C(8)–C(9)–O(10)	120.4(5)	121.2(2)	122(2)	120(2)	123(2)	121(2)
C(8)–C(9)–O(11)	118.1(5)	114.8(2)	119(2)	118(2)	148(2)	116(2)
O(10)–C(9)–O(11)	121.1(5)	124.1(3)	119(2)	121(2)	123(2)	122(2)

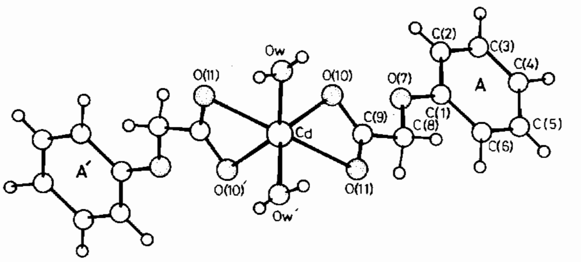

Fig. 1. Molecular configuration and atom naming scheme for $[Cd(PA)_2(H_2O)_2]$ (1).

is six-coordinate and polymeric [14]. With (1), the ligands are less strongly bound to the metal compared to those in $[Zn(PA)_2(H_2O)_2]$ [1], resulting in more equal but longer bond lengths [mean, 2.313 Å (1), *cf.* 2.149 Å (Zn^{II})]. This allows sufficient relief in the steric strain imposed by the phenoxyacetate system for the ligand to acquire the symmetrical disposition observed. Similar relief is seen as the reason for the symmetry of the bidentate PTA chelate ligand in $[Zn(PTA)_2(H_2O)_2]$ [14] via longer S–C distances, and for the unidentate mode with the more sterically crowded 2,4-dichlorophenoxyacetato ligands in the Zn-2,4-D complex [6].

Examples having analogous four membered bidentate rings with distorted six-coordinate geometry are found for cadmium in aqua-(L-glutamato)-cadmium(II) hydrate [19] (metal to bidentate-O: 2.288, 2.252 and 2.317, 2.458 Å; metal–H_2O: 2.258 Å); dichlorobis(glycylglycine)cadmium(II) [19]; (metal to bidentate-O: 2.277, 2.867 and 2.331, 2.435 Å; metal–H_2O: 2.290 Å); and bis (*p* - hydroxybenzoato) tris (pyridine) cadmium (II)· pyridine [20] (metal to bidentate-O: 2.289, 2.502 Å]. However, other stereochemistries are possible such as found in the polymeric complex, cadmium malonate monohydrate [21], where each malonate group is bonded to three different cadmium atoms (metal to bidentate-O: 2.501, 2.330, 2.417, 2.398, 2.277, 2.296 Å), each of which has pentagonal bipyramidal coordination with one carboxyl oxygen linked to two different cadmiums. Polymeric cadmium maleate dihydrate [22] contains two independent metal atoms, one having distorted octahedral coordination (metal to unidentate-O: 2.289, 2.285 Å; metal to H_2O, 2.317, 2.281, 2.274, 2.226 Å) and the other very distorted dodocahedral (metal to bidentate-O: 2.550, 2.297, 2.843, 2.287, 2.598, 2.255, 2.782, 2.195 Å). Once again, carboxyl oxygens bridge two different cadmiums. The possible reason this does not occur in the present case is that these last two examples have small chain dicarboxylic acid ligands which are probably more versatile in forming different stereochemical arrangements. The amino acid/peptide complexes [19] are among seven known structures which exhibit a variety of six and seven coordinate systems with the amino acid groups sometimes behaving as bidentate ligands, forming five membered rings.

Packing in the unit cell is shown in Fig. 2. An intermolecular hydrogen-bonding network links the oxygen of the water molecules to both carboxyl oxygens [Ow···O(10), 2.696 Å; Ow···O(11) 2.703 Å] while longer contacts exist between Ow and O(11) (3.183 Å) and another water (3.223 Å). No short intramolecular (O···O) contacts involving Ow are present.

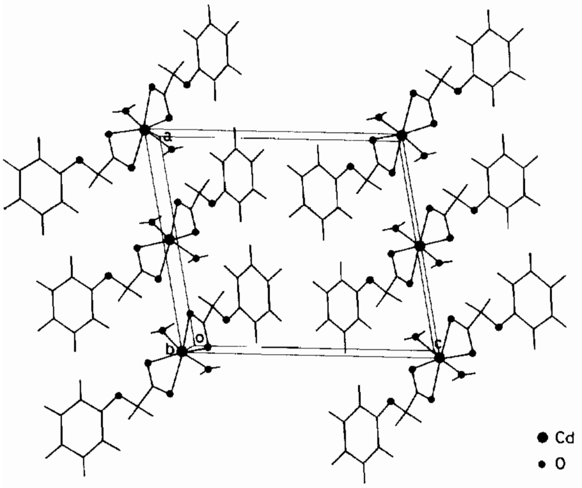

Fig. 2. Packing of (1) viewed perpendicular to the *ac* plane.

[Pb$_2$(PA)$_4$(H$_2$O)]$_n$ (2)

Complex 2 has a two-dimensional polymeric structure, best described in terms of a repeating dimer, with two independent lead centres (Fig. 3). Although this determination lacks the precision of the cadmium complex, the overall stereochemistry has been well defined. Pb(1) is linked to Pb(1)′ [1 − *x*, 1 − *y*, −*z*] across a centre of symmetry through the carboxylate oxygen O(10)B [Pb–O, 2.34(2) Å]. The irregular MO_8 coordination sphere about Pb(1), contains the single water molecule [Pb–Ow, 2.76(2) Å], a carboxylate and an ether oxygen from a B ligand [Pb–O(10)B, 2.51(2) Å; Pb–O(7)B, 2.96(2) Å] in a bidentate chelate mode, and a carboxylate oxygen from another B phenoxyacetate ligand [2.87(2) Å] [1 − *x*, −*y*, −*z*]. The coordination is completed by another oxygen from an A ligand [Pb–O(11)A, 2.71(2) Å (1 − *x*, −*y*, −*z*)]. O(11)A also acts as a bridge to Pb(2) [2.72(2) Å]. Ligand D forms a four-membered ring system with Pb(1) *via* the carboxylate group [Pb(1)–O(10)D, 2.79(2) Å; Pb(1)–O(11)D, 2.51(2) Å] while O(10)D is also bonded to Pb(2) [2.58(2) Å]. On the other hand, Pb(2) is irregular seven-coordinate, but is also linked to another Pb(2) atom (1 − *x*, −*y*, −*z*) through an inversion centre [Pb(2)–O(11)C, 2.73(2)]. The carboxylate groups of both phenoxyacetate ligands A and C form four-membered rings with Pb(2), [Pb(2)–O(10)A, 2.72(2) Å; Pb(2)–O(11)A, 2.58(2) Å; Pb(2)–O(10)C, 2.48(2) Å; Pb(2)–O(11)C, 2.50(2) Å]. The remaining bonds to Pb(2) are from O(10)D [2.57(2) Å] and O(11)B [2.73(2) Å].

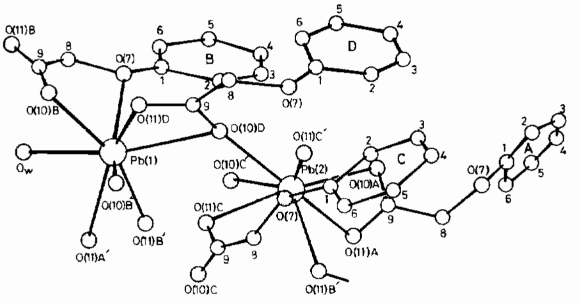

Fig. 3. Molecular configuration and atom naming scheme for [Pb$_2$(PA)$_4$(H$_2$O)]$_n$ (2).

The irregularity found in the coordination about both lead centres in the present structure, as well as the tendency to form polymeric structures is quite common among carboxylate complexes of lead(II). Examples are $[Pb(HCOO)_2\{SC(NH_2)_2\}_2 \cdot H_2O]_n$ (2.59–2.94 Å) [23], $[Pb(CH_3COO)_2\{SC(NH_2)_2\}]_n$ (2.37–3.01 Å) [24], $[Pb(p\text{-}NH_2 \cdot C_6H_4COO)_2]_n$ (2.37–2.84 Å) [25] and $[Pb(p\text{-}NH_2 \cdot C_6H_4COO)(NO_3)]_n$ (2.51–3.07 Å) [26].

Typically, the Pb–O distances are less than 3 Å, the limit imposed in this discussion as the maximum for the polyhedron about Pb. The formation of four-membered chelate ring systems about the Pb centres is also a common feature among the other lead carboxylate examples. However, to date, the only metal(II) phenoxyacetate structures to show this mode of complexation are zinc phenoxyacetate dihydrate (and its isomorphours *p*-chloro analogue) [1] and cadmium phenoxyacetate dihydrate (1). This may reflect the greater steric freedom allowed by the longer M–O bonds associated with Pb. The five-membered chelate ring involving the ether oxygen in this structure (ligand B) is relatively rare outside the Cu^{II} complexes of the phenoxyacetates [1, 27–29], the zinc phenoxyisobutyrate (PIBA) complex, $[Zn_5(PIBA)_{10}(H_2O)_2]_n$ being the only other example [30]. The diminished affinity of the ether oxygen for the metal in (2) is reflected in the longer M–O bond distance and is consistent with the observations for the Cu^{II} complexes where O(ether) invariably occupies the tetragonally elongated axial positions of the coordination sphere. Similarly, the elongated Zn–O distances in the zinc phenoxyisobutyrate complex (both octahedral and trigonal bipyramidal) are associated with the ether oxygens of the PIBA ligands.

The polymer chains of (2) form down the *b* direction in the unit cell (Fig. 4) with no inter-chain stabilization from hydrogen bonding interactions. The water molecule is involved in intermolecular hydrogen bonding to O(10)A (2.80 Å; $1 - x, y, z$), O(10)B (2.94 Å; $x, 1 - y, z$) and O(11)D (2.79 Å; $1 + x, y, z$). Other associations involving carboxyl oxygens only are O(10)B···O(11)D (2.92 Å; $1 - x, 1 - y, z$); O(10)D···O(11)C (2.94 Å; $1 - x, y, z$) and O(11)C···O(11)C′ (2.79 Å; $1 - x, y, z$).

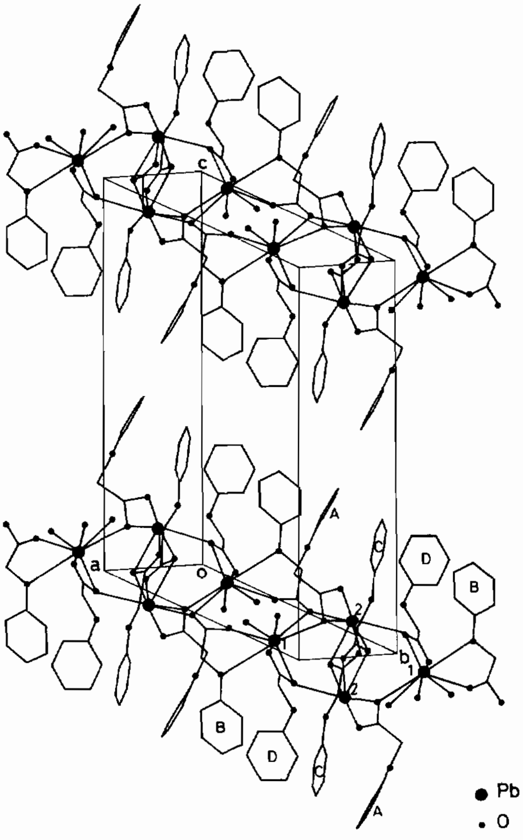

Fig. 4. Packing of (2) in the cell viewed perpendicular to *bc*.

Acknowledgements

The authors thank the University of Queensland and the Queensland Institute of Technology for financial support and the use of computing facilities and the Chinese University of Hong Kong for the use of the diffractometer.

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