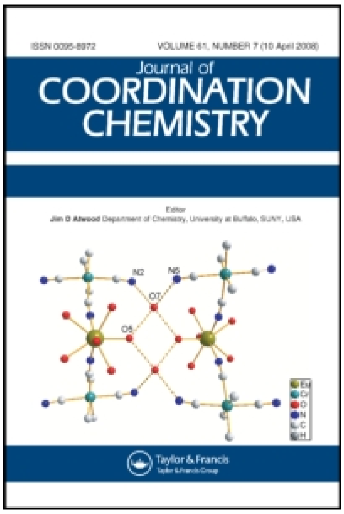

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A Novel Lead- bis (4-Chloro-2-Methylphenoxy)- Acetate Polymeric Complex

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A NOVEL LEAD-*BIS*(4-CHLORO-2-METHYLPHENOXY)-ACETATE POLYMERIC COMPLEX

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The *bis*(4-chloro-2-methylphenoxy)acetato lead (II) monohydrate infinite polymer was synthesized and characterized by elemental analysis and infrared spectroscopy. The crystal and molecular structure has been determined and the bond valences were computed. Molecules of the monomer, each occupying an asymmetric unit, are connected by the inversion center and a polymer chain is created by Pb(2O)Pb rings in *spiro* arrangement. The lead atom is seven coordinate by four oxygen atoms from two chelating carboxyl groups, one water molecule, and two oxygen atoms provided by symmetry generated carboxyl groups. Each carboxyl group acts as a bidentate ligand toward one metal atom and as a monodentate ligand with respect to a second. The lead–oxygen distances are spread over a wide range of values. One molecule of (4-chloro-2-methylphenoxy)acetate in the monomer is close to planarity, and the second is bent. All 4-chloro-2-methylphenoxy groups are almost parallel. The polymer infinite chains are assembled by weak hydrogen bonds to a layered structure.

Keywords: Inorganic polymer; Seven-coordinate lead (II); Bond valence

INTRODUCTION

The problem posed by contamination of the environment by heavy metals such as cadmium, lead, copper, or mercury, is of outstanding importance. Amongst these metals much of the attention in recent years has focused on lead [1], due to its extensive industrial use and its toxicity to humans [2,3]. Even if decreased use of leaded gasoline has reduced the release of lead into atmosphere, other anthropogenic sources of lead contamination are pigment making, lead battery manufacturing, and especially, their disposal. The study of the coordination chemistry of lead has been of crucial importance over the last few years in the search for chelating agents, which may serve as metal-sequestering agents not only for environmental applications but also for biomedical purposes [1,4–6].

The molecule (4-chloro-2-methylphenoxy)acetic acid (MCPA), is an important commercial herbicide of the phenoxyalkanoic acid series. The herbicides not only affect

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weeds but also can react with metals, which contaminate soil. Now we report on the synthesis and structural characterization of the lead complex with MCPA. Its structure has revealed an unusual binding behavior of the carboxylic group toward the lead atom. We believe that this compound may provide useful information on blocking lead in soil [unpublished results] and prevent it from being assimilated by crops.

EXPERIMENTAL

Preparation of $Pb(MCPA)_2 \cdot H_2O$

The MCPA (purity 96.1%, produced by Organika-Sarzyna, Poland) was purified by recrystallization from a water–ethanol solution in ratio 1 : 1 (V/V). Pure MCPA (0.500 g, 2.50 mmol) was dissolved in water with addition of solid NaOH (the final pH of solution was 5–7). An aqueous solution of $Pb(NO_3)_2$ (0.414 g, 1.25 mmol) was mixed with the MCPA solution (the ligand: metal molar ratio – 2 : 1) and left for 24 h. A precipitated fine white crystalline compound, was filtered, washed with water and dried at room temperature (yield 75%). The composition of the salt, $Pb(MCPA)_2 \cdot H_2O$, was determined by chemical analysis of lead (II) (complexometric titration with EDTA) and elemental analysis (carbon, chloride and hydrogen). Analytical data (calculated/found): Pb, 33.19/31.79%; C, 34.63/34.57%; H, 2.88/2.83%; Cl, 11.36/9.35%. The solubilities in water and 1 M HCl (at 293 K) calculated on the basis of lead(II) determination in the saturated solutions were 5.8×10^{-4} M and 3.7×10^{-3} M, respectively.

A 0.005 g (0.008 mmol) sample of the product was dissolved in 10 mL of water with 2 mL of ethanol (96% V/V) at 80°C. The solution was filtered, covered and stored at 5°C. After three months thin plate-shaped crystals had grown.

X-ray Crystal Structure Analysis

A thin plate crystal, cut from a larger plate, of the title compound of approximate dimensions $0.028 \times 0.194 \times 0.319$ mm was mounted on a KM-4-CCD automatic diffractometer equipped with a CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at room temperature with ω scan mode. A 37 s exposure time was used. A half of Ewald sphere was collected. The unit cell parameters were determined from least-squares refinement of the setting angles of the 4825 strongest reflections. Details concerning crystal data and refinement are given in Table I.

Examination of two reference frames monitored after each 50 frames measured showed 0.07% loss of the intensity. During the data reduction a decay correction coefficient was taken into account. The Lorentz-polarization correction was applied to the intensity data. A numerical absorption correction was also used. The maximum and minimum transmission factors were 0.795 and 0.170, respectively.

The mean value of $|E^2 - 1|$ statistics was 0.678 (expected 0.968 for centrosymmetric and 0.736 for non-centrosymmetric structure), therefore the space group $P1$ was assigned and the structure of the title compound was solved by direct methods and subsequently completed by difference Fourier recycling. After the end of refinement it was found that two monomers of the title compound are connected by a symmetry center.

TABLE I Crystal data and structure refinement for title compound

Empirical formula	$(C_{18}H_{18}Cl_2O_7Pb)_n$
Formula weight	624.41
Temperature	293(2) K
Wavelength	$\lambda(MoK\alpha) = 0.71073$ Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	$a = 7.964(2)$ $b = 8.366(2)$ $c = 17.160(3)$ Å $\alpha = 99.91(3)$ $\beta = 90.63(3)$ $\gamma = 115.08(3)^\circ$
Volume	1015.5(4) $Å^3$
Z, calculated density	2, 2.042 Mg/m^3
Absorption coefficient	8.607 mm^{-1}
$F(000)$	596
Crystal size	0.03 × 0.19 × 0.32 mm
θ range for data collection	3.31–25.15°
Index ranges	$-9 \leq h \leq 9$, $-9 \leq k \leq 10$, $-20 \leq l \leq 20$
Reflections collected/unique	10059/3631 [R(int) = 0.0712]
Completeness to $\theta = 25.15^\circ$	99.7%
Refinement method	full-matrix least-squares on F^2
Max. and min. transmission	0.795 and 0.170
Data/restraints/parameters	3631/0/307
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0373$, $wR2 = 0.0900$
R indices (all data)	$R1 = 0.0392$, $wR2 = 0.0919$
Largest diff. peak and hole	1.472 and −0.922 e. $Å^{-3}$

Marsh has pointed out that it is extremely difficult to decide by diffraction methods whether a crystal structure is centrosymmetric or only approximately so [7,8]. In addition Marsh has argued that the $|E^2 - 1|$ statistical test can be very deceptive [8]. Watkin and Marsh recommend describing any structure in a centrosymmetric space group if at all possible, for centrosymmetric refinement will not suffer from near-singularities and should converge normally [8,9]. Therefore, the structure was solved in centrosymmetric $P\bar{1}$ space group. The structure of the title compound was solved by the Patterson superposition procedure and subsequently completed by the difference Fourier recycling.

All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2. All the hydrogen atoms were found from a difference Fourier synthesis after four cycles of anisotropic refinement, and their positional parameters were free to refine. The solution and refinements were performed with SHELXS97 [10] and SHELXL97 [11]. The graphical manipulations were performed using the XP routine of the SHELXTL [12] and ORTEP [13]. Atomic scattering factors were those incorporated in the computer programs. Interatomic bond distances and angles are listed in Table II. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table III.

Physical Measurements

The IR spectrum of $Pb(MCPA)_2 \cdot H_2O$ was recorded on a Shimadzu 8501 FTIR spectrometer using a KBr pellet (cm^{-3}): 3408 s, 3230 w, 2924 m, 2361 s, 1603 vs, 1549 vs, 1522 vs, 1491 vs, 1445 vs, 1433 vs, 1410 vs, 1340 s, 1296 vs, 1275 w, 1261 s, 1242 s, 1232 vs,

TABLE II Bond lengths [Å], bond angles and torsion angles [deg.]

1		*2*	
Bond lengths			
Pb(1)–O(3)	2.419(5)	Pb(1)–O(13)	2.507(5)
Pb(1)–O(2)	2.613(5)	Pb(1)–O(12)	2.657(5)
Pb(1)–O(3)#1	2.649(4)	Pb(1)–O(13)#2	2.717(4)
C(1)–O(1)	1.385(8)	C(11)–O(11)	1.377(9)
C(1)–C(6)	1.386(11)	C(11)–C(16)	1.380(10)
C(1)–C(2)	1.394(10)	C(11)–C(12)	1.407(10)
C(2)–C(3)	1.378(11)	C(12)–C(13)	1.390(11)
C(2)–C(7)	1.500(11)	C(12)–C(17)	1.497(11)
C(3)–C(4)	1.379(13)	C(13)–C(14)	1.376(12)
C(4)–C(5)	1.371(13)	C(14)–C(15)	1.371(12)
C(4)–Cl(1)	1.738(8)	C(14)–Cl(11)	1.746(9)
C(5)–C(6)	1.391(12)	C(15)–C(16)	1.388(12)
O(1)–C(8)	1.432(8)	O(11)–C(18)	1.410(8)
C(8)–C(9)	1.523(9)	C(18)–C(19)	1.520(10)
C(9)–O(2)	1.232(8)	C(19)–O(12)	1.246(8)
C(9)–O(3)	1.268(8)	C(19)–O(13)	1.264(8)
O(3)–Pb(1)#1	2.649(4)	O(13)–Pb(1)#2	2.717(4)
Pb(1)–O(4)	2.774(6)		
Bond angles			
O(3)–Pb(1)–O(13)	77.42(16)		
O(13)–Pb(1)–O(2)	74.95(17)		
O(13)–Pb(1)–O(3)#1	118.57(15)		
O(3)–Pb(1)–O(12)	74.53(16)		
O(2)–Pb(1)–O(12)	110.11(16)		
O(3)#1–Pb(1)–O(12)	72.44(15)		
O(3)–Pb(1)–O(13)#2	125.54(15)		
O(2)–Pb(1)–O(13)#2	83.04(16)		
O(3)#1–Pb(1)–O(13)#2	164.56(16)		
O(4)–Pb(1)–O(2)	70.48(18)	O(4)–Pb(1)–O(12)	147.80(16)
O(4)–Pb(1)–O(3)	82.88(18)	O(4)–Pb(1)–O(13)	145.35(18)
O(4)–Pb(1)–O(3_$2)	77.68(16)	O(4)–Pb(1)–O(13_$5)	111.47(16)
O(3)–Pb(1)–O(2)	51.51(15)	O(13)–Pb(1)–O(12)	50.29(15)
O(3)–Pb(1)–O(3)#1	66.61(17)	O(13)–Pb(1)–O(13)#2	61.17(17)
O(2)–Pb(1)–O(3)#1	112.14(14)	O(12)–Pb(1)–O(13)#2	100.36(15)
O(1)–C(1)–C(6)	122.9(6)	O(11)–C(11)–C(16)	124.6(6)
O(1)–C(1)–C(2)	116.2(6)	O(11)–C(11)–C(12)	115.1(6)
C(6)–C(1)–C(2)	121.0(7)	C(16)–C(11)–C(12)	120.4(7)
C(3)–C(2)–C(1)	118.1(7)	C(13)–C(12)–C(11)	117.7(7)
C(3)–C(2)–C(7)	121.4(7)	C(13)–C(12)–C(17)	120.0(7)
C(1)–C(2)–C(7)	120.5(7)	C(11)–C(12)–C(17)	122.3(7)
C(2)–C(3)–C(4)	121.1(8)	C(12)–C(13)–C(14)	121.0(8)
C(5)–C(4)–C(3)	120.9(7)	C(15)–C(14)–C(13)	121.4(8)
C(5)–C(4)–Cl(1)	119.8(7)	C(15)–C(14)–Cl(11)	119.2(7)
C(3)–C(4)–Cl(1)	119.2(7)	C(13)–C(14)–Cl(11)	119.4(7)
C(4)–C(5)–C(6)	119.0(8)	C(14)–C(15)–C(16)	118.5(8)
C(1)–C(6)–C(5)	119.9(8)	C(11)–C(16)–C(15)	121.1(7)
C(1)–O(1)–C(8)	114.8(5)	C(11)–O(11)–C(18)	117.9(6)
O(1)–C(8)–C(9)	109.4(5)	O(11)–C(18)–C(19)	113.2(6)
O(2)–C(9)–O(3)	122.7(6)	O(12)–C(19)–O(13)	122.3(6)
O(2)–C(9)–C(8)	118.6(6)	O(12)–C(19)–C(18)	119.6(6)
O(3)–C(9)–C(8)	118.7(6)	O(13)–C(19)–C(18)	118.1(6)
C(9)–O(2)–Pb(1)	88.7(4)	C(19)–O(12)–Pb(1)	90.4(4)
C(9)–O(3)–Pb(1)	97.0(4)	C(19)–O(13)–Pb(1)	97.0(4)
C(9)–O(3)–Pb(1)#1	139.1(4)	C(19)–O(13)–Pb(1)#2	124.8(4)
Pb(1)–O(3)–Pb(1)#1	113.39(17)	Pb(1)–O(13)–Pb(1)#2	118.83(17)

(*Continued*)

TABLE II (*Continued*)

1		*2*	
Torsion angles			
C(5)–C(6)–C(1)–O(1)	179.3(8)	C(15)–C(16)–C(11)–O(11)	−177.4(7)
C(6)–C(1)–O(1)–C(8)	−25.1(10)	C(16)–C(11)–O(11)–C(18)	−4.5(10)
C(1)–O(1)–C(8)–C(9)	−167.4(6)	C(11)–O(11)–C(18)–C(19)	76.7(8)
O(1)–C(8)–C(9)–O(3)	−28.2(8)	O(11)–C(18)–C(19)–O(13)	13.7(10)
C(3)–C(2)–C(1)–O(1)	−179.1(7)	C(13)–C(12)–C(11)–O(11)	177.1(7)
C(2)–C(1)–O(1)–C(8)	156.0(6)	C(12)–C(11)–O(11)–C(18)	176.1(6)
C(1)–O(1)–C(8)–C(9)	−167.4(6)	C(11)–O(11)–C(18)–C(19)	76.7(8)
O(1)–C(8)–C(9)–O(2)	154.4(6)	O(11)–C(18)–C(19)–O(12)	−167.0(6)
C(7)–C(2)–C(1)–O(1)	−0.4(11)	C(17)–C(12)–C(11)–O(11)	−1.4(11)

Symmetry transformations used to generate equivalent atoms: #1 $-x,-y+1,-z$; #2 $-x+1,-y+1,-z$.

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for title compound. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	X/a	Y/b	Z/c	$U_{(eq)}$
Pb(1)	2302(1)	4732(1)	487(1)	36(1)
C(1)	−3362(9)	930(9)	−2642(4)	43(2)
C(2)	−5185(10)	746(10)	−2637(5)	47(2)
C(3)	−6427(11)	−326(11)	−3285(5)	56(2)
C(4)	−5879(13)	−1165(12)	−3927(5)	63(2)
C(5)	−4080(14)	−967(15)	−3938(5)	69(2)
C(6)	−2801(12)	103(13)	−3289(5)	61(2)
C(7)	−5772(13)	1662(14)	−1937(6)	58(2)
Cl(1)	−7519(5)	−2559(5)	−4714(2)	107(1)
O(1)	−2167(6)	1997(7)	−1974(3)	46(1)
C(8)	−612(9)	1612(10)	−1837(4)	40(1)
C(9)	333(8)	2561(8)	−1005(4)	35(1)
O(2)	1223(7)	1931(7)	−671(3)	47(1)
O(3)	231(6)	4003(6)	−695(3)	41(1)
O(4)	−678(8)	1868(8)	905(4)	55(1)
C(11)	5151(10)	6351(9)	−2311(4)	41(1)
C(12)	5965(10)	5585(10)	−2894(4)	46(2)
C(13)	4804(12)	4343(12)	−3541(5)	58(2)
C(14)	2931(12)	3908(13)	−3613(5)	62(2)
C(15)	2142(12)	4685(12)	−3055(5)	58(2)
C(16)	3275(11)	5919(11)	−2402(5)	48(2)
C(17)	7997(12)	6032(15)	−2826(6)	65(2)
Cl(11)	1522(4)	2320(5)	−4430(2)	100(1)
O(11)	6351(7)	7507(7)	−1667(3)	47(1)
C(18)	5648(12)	8407(10)	−1085(4)	49(2)
C(19)	4462(8)	7214(9)	−538(4)	36(1)
O(12)	3485(7)	7731(7)	−96(3)	46(1)
O(13)	4522(6)	5726(7)	−546(3)	45(1)

1188 vs, 1138 vs, 1097 w, 1069 s, 1053 s, 993 w, 947 w, 883 s, 874 s, 808 s, 799 s, 791 s, 756 m, 714 s, 669 w, 650 s, 604 m, 554 w, 515 w, 442 w, 419 w (vs = very strong, s = strong, m = medium, w = weak). The IR spectrum of the complex can be divided into regions [14–16]: 3400–2900 cm^{-1} stretching vibrations of the OH-group (from water); 1610–1300 cm^{-1} the C–O stretching of the carboxyl group (ν_{asym}, ν_{sym}), aromatic C–C stretching vibrations, deformation vibrations of water molecules; 1275–1200 cm^{-1} the Ar–O–C stretching vibrations (antisymmetrical); 1200–1050 cm^{-1} the Ar–O–C stretching vibrations (symmetrical) and bending in the C–H–C plane in the substituted aromatic ring; 880–400 cm^{-1} the deformation vibrations of M–OH_2 and carboxyl group, bending in the benzene ring and stretching of M–O (in the aqua-complex). Many peaks in the IR spectrum of $Pb(MCPA)_2 \cdot H_2O$ are caused by the ligand (MCPA). For the lead(II) complex, new peaks of coordinated water molecule are observed. Very strong peaks of two C–O stretching vibrations ν_{asym} at 1548 and 1522 cm^{-1} and ν_{sym} at 1445, 1433 and 1410 cm^{-1} are broadened and shifted to lower energies. These can be explained by withdrawal of the electron density from carboxyl oxygen atoms towards the metal atom. There are both chelating and bridging carboxyl groups in the complex.

RESULTS AND DISCUSSION

A perspective view of the structure together with the atom numbering scheme is shown in Fig. 1, hydrogen atoms being omitted for clarity. The structure is plotted with 50% probability displacement ellipsoids.

The lead atom is seven-coordinate with four oxygen atoms from two chelating carboxyl groups, one water molecule, and two oxygen atoms provided by $-x,-y+1,-z$ and $-x+1,-y+1,-z$ symmetry generated carboxyl groups from adjacent units, which means that each carboxyl group acts as bidentate ligand toward one metal and as a monodentate ligand with respect to a second. Conversely, a carboxyl group, symmetry related to the latter, donates one oxygen atom to the first lead atom considered. In this manner infinite polymer chains with the $Pb(C_9H_8ClO_3,H_2O)_2$ repeat unit are formed parallel to the crystallographic x axis. The successive monomers, each occupying an asymmetric unit, are connected by an inversion center, which leads to a polymer chain created by Pb(2O)Pb rings in a *spiro* arrangement (Fig. 2). There is no polymer of this type (Fig. 3a) reported in the literature. All lead–carboxyl polymers described so far are in a fuse arrangement [17–19] (Fig. 3b), and this arrangement is observed also for dimers [1, 20–23].

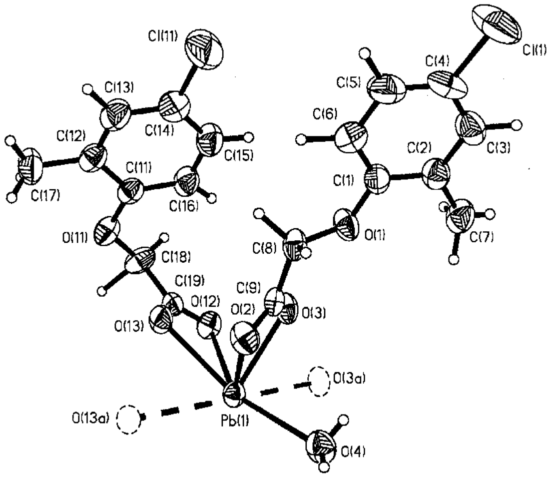

FIGURE 1 The molecular conformation of the monomer unit of the title compound with atom numbering, plotted with 50% probability of displacement ellipsoids. The symmetry equivalent atoms are indicated by dashed lines.

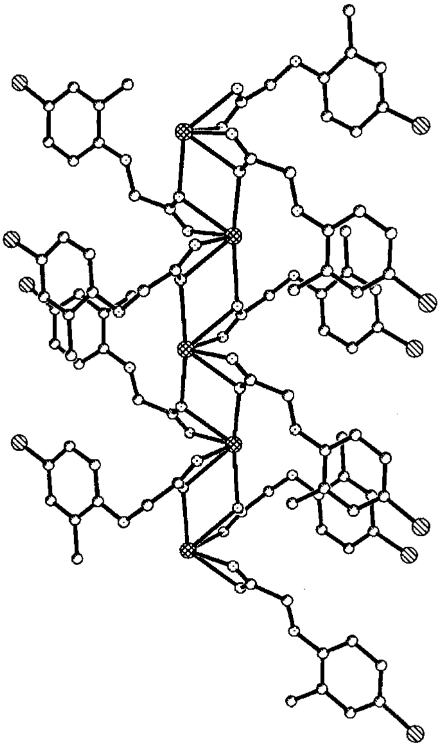

FIGURE 2 Fragment of infinite polymer chain created by rings in *spiro* arrangement along *z*-axis. Hydrogen atoms being omitted for clarity.

The lead atom adopts a mixed trigonal–tetragonal antiprism (4 + 3) coordination (Fig. 4). The O(4), O(3a), O(12) and O(13a) atoms (O(3a) and O(13a) obtained by $-x,-y+1,-z$ and $-x+1,-y+1,-z$ symmetry transformations, respectively) are close to planarity, with maximum deviation 0.308(3) Å for O(3a) atom. These planes make dihedral angles of 80.9(6)° and 33.9(8)° with the least squares planes calculated through carboxylate groups and angles 82.4(2)° and 33.7(3)° with the least squares planes calculated through acetate groups indicated by C(9) and C(19) atoms, respectively. For chelating carboxyl groups considered as a single coordination entity (the coordination bisecting O–C–O) leads to a distorted tetragonal pyramid (4 + 1) coordination at lead. As shown on Fig. 4, one side of the lead coordination polyhedron is unoccupied. Such an arrangement is imposed by the steric effect of methyl groups (Pb(1)–C(7#$-x,-y+1,-z$) distance equal to 3.623(11) Å and Pb(1)–C(17#$-x+1,-y+1,-z$) equal to 4.165(11) Å).

The lead–oxygen atom distances are spread over a wide range of values, essentially as is found for other lead complexes with related ligands [1,17–28], and can be compared to those found for other lead carboxylates (2.32–2.79 Å) [24,25], and those formed by a chelating acetate (mean value 2.49 Å [26]). The bond valences were computed as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/B]$ [29–31], where R_{ij} is the bond–valence parameter (in the formal sense R_{ij} is the single-bond length between i and j atoms) [32]. The $R_{\text{Pb–O}}$ was taken as 2.112 [33] and the value of B was taken as 0.39 according to distances observed in similar compounds [27,28]. The computed bond valences of the

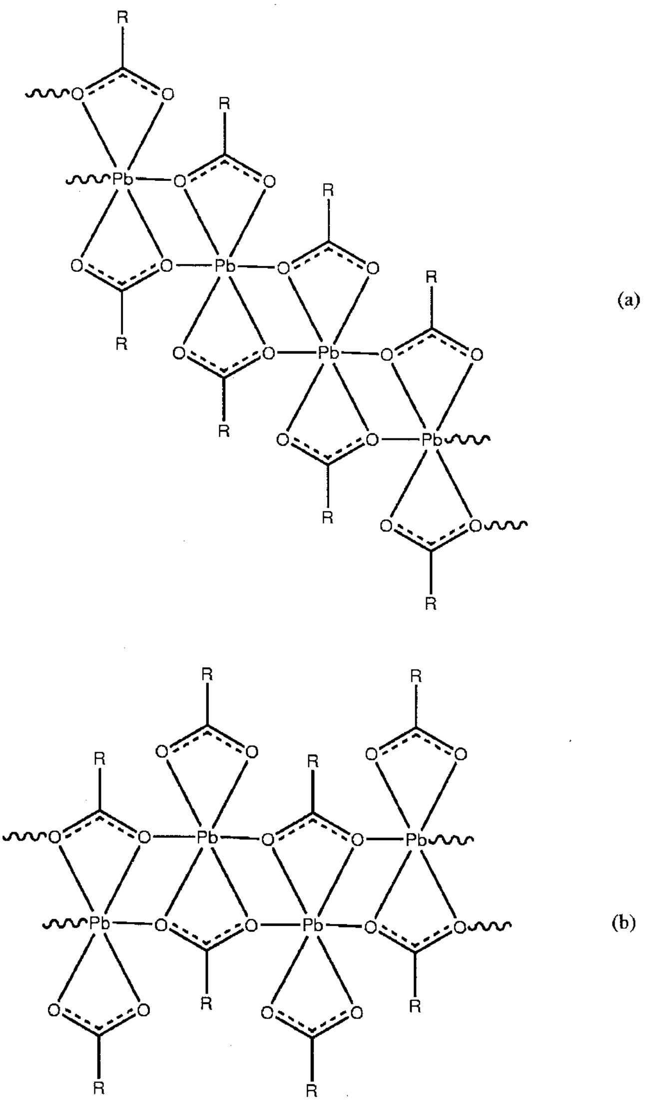

FIGURE 3 Lead–carboxylate polymer chain created by Pb(2O)Pb rings: (a) in a *spiro* arrangement (this work), (b) in a fuse arrangement (previously reported polymeric structures).

lead are $\nu_{\mathrm{Pb(1)–O(2)}} = 0.277$, $\nu_{\mathrm{Pb(1)–O(3)}} = 0.455$, $\nu_{\mathrm{Pb(1)–O(3a)}} = 0.252$, $\nu_{\mathrm{Pb(1)–O(12)}} = 0.247$, $\nu_{\mathrm{Pb(1)–O(13)}} = 0.363$, $\nu_{\mathrm{Pb(1)–O(13a)}} = 0.212$ and $\nu_{\mathrm{Pb(1)\text{-}O(4)}} = 0.183$ v.u. (valence units). The valence sum rule states that the sum of the valences of the bonds formed by an atom is equal to the valence of the atom, thus the computed valence of the Pb(1) atom is 1.989 v.u., which agrees with the formal oxidation state of the lead. This confirms that the water molecule indicated by O(4) atom is included in the coordination sphere of lead, because only a violation of the valence-sum rule can indicate mistakes in the interpretation of a structure by the omission or addition of any bonds [32,34]. For oxygen carbon bond valences the $R_{\mathrm{O–C}}$ was taken as 1.41 (mean value of bond–valence parameters taken from references [32,33]) and the value of B was taken as

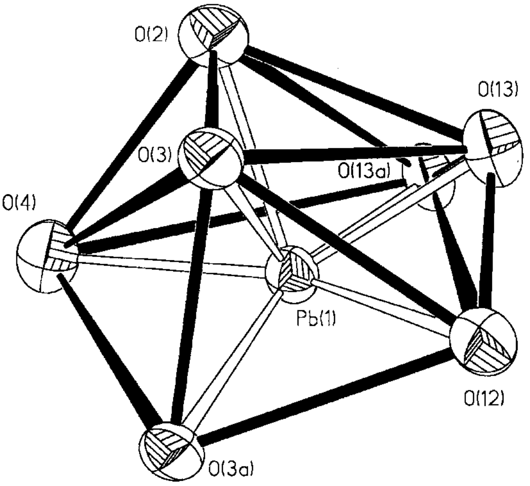

FIGURE 4 The lead polyhedra.

TABLE IV Hydrogen-bonds for title compound [distances in Å and angles in deg.]

D–H...A	*d(D–H)*	*d(H...A)*	*d(D...A)*	< (*DHA*)
O(4)–H(4O)...O(2)#3	0.87(9)	2.15(9)	2.973(8)	158(8)
O(4)–H(4P)...O(12)#1	0.81(9)	2.02(9)	2.787(8)	160(8)
O(4)–H(4P)...O(3)	0.81(9)	3.05(9)	3.448(8)	113(7)
C(5)–H(5)...Cl(11)#4	1.02(8)	2.77(8)	3.778(10)	167(6)
C(8)–H(8B)...O(11)#5	0.98(8)	2.45(9)	3.324(9)	148(6)

Symmetry transformations used to generate equivalent atoms:
#1 $-x,-y+1,-z$; #2 $-x+1,-y+1,-z$; #3 $-x,-y,-z$; #4 $-x,-y,-z-1$; #5 $x-1, y-1, z$.

0.37 [32,35]. The computed bond valences are $\nu_{O(2)-C(9)} = 1.578$, $\nu_{O(3)-C(9)} = 1.439$, $\nu_{O(12)-C(19)} = 1.523$ and $\nu_{O(13)-C(19)} = 1.454$ v.u. Hydrogen acceptor valences ($\nu_{O\ldots H}$) were obtained from O–O bond distance versus bond valence relationship [36]. Valences of the carboxylate oxygen atoms are 1.99, 2.15, 1.99 and 2.03 v.u. for O(2), O(3), O(12) and O(13) atoms, respectively. It has been stated that the bond valence represents a measure of the strength of a bond that is independent of the atomic size [37]. The application of this correlation implies that the MPCA molecule indicated by C(1) atom (**I** hereafter) is more strongly bound to the lead atom than the MPCA molecule indicated by C(11) atom (**II** hereafter, valences of (**I**) are always larger than respective valences of (**II**)). The complex is stabilized by the presence of hydrogen bonding between the carboxylate oxygen atoms and the bonded water (for details see Table IV). The bond distances and angles within the MPCA molecules are comparable to those found for the free acid [38] and its complexes with Mg [39], Zn [40], and Mn [41]. The major difference between the discussed compound and compounds reported in the literature is the side chain conformation, best illustrated by the values of torsion angles about the oxygen atom from the phenoxy group and the adjacent acetate carbon atom. In the close of planar MPCA molecule, this angle is +173.5° [38] and in manganese complex it is −80.1° [39]. Here we found −167.4(6)° and 76.7(8)°, for (**I**) and (**II**), respectively. This means that overall arrangement of each of the MPCA molecules is close to that reported in the literature but this association of conformations

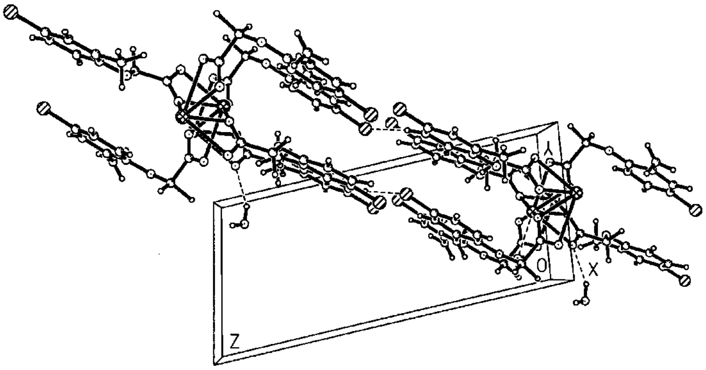

FIGURE 5 Fragment of crystal packing of title compound showing infinite layer created by hydrogen bounded polymer chains.

in one structure is not typical. The least squares planes calculated through the acetate groups of (**I**) and (**II**) make a dihedral angle of 71.3(3)° and through the carboxylate groups make an angle 72.5(6)°. The benzene rings of (**I**) and (**II**) are planar within experimental error and form a dihedral angle 5.4(4)°. However, the distance between (**I**) and the obtained by $x+1$, $y+1$, z symmetry transformation of (**II**) benzene rings centroids is rather short (3.798(5) Å) and the angle between interring vector and normal to benzene plane of plane (**I**) amounts to 17.2(4)°. The possibility of stacking of π electrons was rejected because rings are inclined at 5.3(3)°. The 4-chloro-2-methylphenoxy group of (**I**) is close to planar (maximum deviation of −0.036(5) Å for Cl(1) atom) and makes a dihedral angle 4.9(3)° with the least squares plane calculated through the respective atoms of ligand (**II**) (maximum deviation of −0.048(5) Å for O(11) atom). The shortest lead-lead distance is 4.2376(12) Å (second) lead atom obtained by $-x$, $-y+1$, $-z$ symmetry transformation).

The infinite polymer chains are assembled by weak hydrogen bonds to give a layered structure (Fig. 5, Table IV). Creation of these layers, together with parallel placement of 4-chloro-2-methylphenoxy groups explains the morphology of thin plates that are observed rather than the rectangular prisms expected for the obtained unit cell dimensions.

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Supporting Information Available

Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under No. CCDC161001.

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