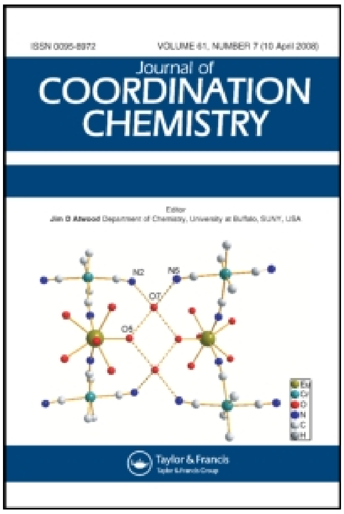

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A novel polymeric (4-chloro-2-methylphenoxy) acetate complex of cadmium(II)

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A NOVEL POLYMERIC (4-CHLORO-2-METHYLPHENOXY) ACETATE COMPLEX OF CADMIUM(II)

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The infinite, two-dimensional polymer *bis*[(4-chloro-2-methylphenoxy)acetato] cadmium dihydrate was synthesized and characterized by elemental analysis and infrared spectroscopy. The crystal and molecular structure has been determined. The cadmium atom is six coordinated by four oxygen atoms from bridging carboxyl groups and two oxygen atoms from water molecules. The polymer net is stabilized by two O–H···O hydrogen bonds. Bond distances and angles within MCPA molecules are comparable to those found for the free acid and its complexes. The shortest cadmium–cadmium distance is 5.453(1) Å.

Keywords: Metal-organic polymer; Cadmium; Bond valence; X-ray structure

INTRODUCTION

The problems posed by environment contamination by heavy metals such as cadmium, lead, copper and mercury are of outstanding importance. Among these metals, much attention in recent years has focused on cadmium, due to its extensive industrial use, carcinogenic properties and toxicity to humans [1,2]. Even if use of anthropogenic sources of cadmium, such as nickel–cadmium batteries or production of bearing alloys were decreased, cadmium may continue to pollute the environment as a result of zinc production and technical zinc applications. The study of the coordination chemistry of cadmium has been of crucial importance over the last few years in a search for complexing agents that may serve as extractants or blockers of this metal for environmental or recycling purposes. The development of such technologies will rely on the ability of a compound selectively or specifically to bind a metal ion, or ion types [3]. Cadmium is well known to form complexes with acetates and carboxy-ligands to yield both charged and neutral compounds [4]. The possibility of forming structures with higher coordination numbers has resulted in the observation of unusual coordination geometries about the metal atom and formation of polymeric species [4,5].

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The compound (4-chloro-2-methylphenoxy)acetic acid (MCPA) is an important commercial herbicide of the phenoxyalkanoic acid series. The herbicides not only affect weeds but can react with metals that contaminate soil. We report the synthesis and structural characterization of a cadmium complex with MCPA. Its structure has revealed rather sporadically spotted binding behavior of the carboxylic group towards the cadmium atom. We believe that this compound may provide useful information on blocking cadmium in soil and in preventing it from being assimilated by crops.

EXPERIMENTAL

Synthesis

The ligand (4-chloro-2-methylphenoxy)acetic acid, MCPA (purity 96.1%, produced by Organika-Sarzyna, Poland), was purified by recrystallization from water–ethanol. After purification MCPA was dissolved in water with addition of solid NaOH (the final pH was 5–7). An aqueous solution of $Cd(NO_3)_2$ was added (ligand:metal 2:1) and left for 24 h. The white, finely crystalline compound that formed was filtered, washed with water and dried at room temperature. Crystals of $Cd(MCPA)_2 \cdot 2H_2O$ were obtained from a saturated water–ethanol solution (5:1 v/v) by slow evaporation at room temperature. After three months when very thin, plate-shaped crystals had grown, a few drops of ethyl acetate were added to the solution (to lower the solubility of the compound). After one month thin, plate-shaped crystals suitable for X-ray crystallography were obtained. The composition of the salt, $Cd(MCPA)_2 \cdot 2H_2O$, was determined by chemical analysis of cadmium(II) (complexometric titration with EDTA) and elemental analysis (carbon, chloride and hydrogen). Anal. Calcd. (%): Cd, 20.5; C, 39.5; H, 3.7; Cl, 13.0. Found: Cd, 20.3; C, 39.4; H, 3.7; Cl, 10.4. The solubility of the salt in water (293 K) calculated on the basis of cadmium(II) determination in a saturated solution is $7.2 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$.

X-ray Crystal Structure Analysis

A thin crystal, cut from a larger plate, of approximate dimensions $0.083 \times 0.250 \times 0.403$ 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 the ω scan mode. A 20 s exposure time was used. A whole Ewald sphere up to $\theta = 25°$ was collected. Unit cell parameters were determined from least-squares refinement of the setting angles of 4018 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 a 2.12% increase in the intensity. During data reduction, this was taken into account. A Lorentz–polarization correction was applied to the data and a numerical absorption correction was used [6]. Maximum and minimum transmission factors were 0.916 and 0.515.

The structure of the complex was solved by the Patterson method and subsequent difference Fourier cycles. All nonhydrogen atoms were refined anisotropically using full-matrix, least-squares techniques on F^2. All hydrogen atoms were found from a difference Fourier synthesis after four cycles of anisotropic refinement and their posi-

TABLE 1 Crystal data and structure refinement for the complex

Empirical formula	$(C_{18}H_{20}CdCl_2O_8)_n$
Formula weight	547.64
Temperature (K)	291(1)
Wavelength (Å)	$\lambda(\mathrm{Mo}K\alpha) = 0.71073$
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions (Å,°)	$a = 17.9797(9)$ $b = 7.2044(4)$ $c = 8.1885(5)$ $\beta = 96.929(5)$
Volume (Å^3)	1052.93(10)
Z, Calculated density (Mg m^{-3})	2, 1.727
Absorption coefficient (mm^{-1})	1.333
$F(000)$	548
Crystal size (mm)	$0.40 \times 0.25 \times 0.08$
θ range for data collection (°)	3.63 to 25.10
Index ranges	$-21 \leq h \leq 21$, $-8 \leq k \leq 8$, $-9 \leq l \leq 8$
Reflections collected/unique	10648/1872 [R(int) = 0.0330]
Completeness to $\theta = 25.15°$ (%)	91.7
Refinement method	full-matrix least-squares on F^2
Max. and min. transmission	0.916 and 0.515
Data/restraints/parameters	1872/0/163
Goodness-of-fit on F^2	1.150
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0271$, $wR2 = 0.0605$
R indices (all data)	$R1 = 0.0278$, $wR2 = 0.0610$
Largest diff. peak and hole(e Å^{-3})	0.350 and −0.378

tional parameters were refined. Solution and refinement were performed with SHELXS97 [7] and SHELXL97 [8]. Graphical manipulations were performed using the XP routine of SHELXTL [9] and ORTEP [10]. 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.

Infrared Spectra

IR spectra of $Cd(MCPA)_2 \cdot 2H_2O$ were recorded on a Shimadzu 8501 FTIR spectrophotometer using KBr pellets. Absorption frequencies were as follows (cm^{-1}): 3410 s, 3240 w, 2950 w, 2920 w, 2361 s, 2343 s, 1605 vs, 1558 m, 1541 m, 1493 vs, 1447 s, 1431 s, 1421 s, 1406 m, 1338 vs, 1302 m, 1271 w, 1244 vs, 1232 s, 1190 vs, 1138 s, 1065 m, 1053 m, 991 w, 949 w, 885 m, 800 s, 793 m, 756 w, 719 m, 669 w, 654 m, 579 w, 555 w, 520 w, 444 w, 419 w (vs = very strong, s = strong, m = medium, w = weak). Many peaks of the complex are similar to those recorded for the ligand. The 3400–2900 cm^{-1} region corresponds to stretching of the OH group from water; 1610–1300 cm^{-1} C–O stretching of the carboxyl group, aromatic C–C stretching and deformation of water molecules; 1275–1050 cm^{-1} Ar–O–C stretching and bending in the C–H–C plane in the substituted aromatic ring; 880–400 cm^{-1} deformation of M–OH_2 and the carboxyl group, bending in the benzene ring and M–O stretching [11]. The acetate group can coordinate to a metal ion as a simple unidentate ligand, an unsymmetrical chelating bidentate group, a symmetrical chelating bidentate group, an unsymmetrical bridging bidentate group and a symmetrical bridging bidentate group [12,13]. The mode of coordination influences the C–O frequencies of the COO

TABLE II Structural data for the title compound. Distances are in Å, angles and torsion angles in deg

Distances	
Cd(1)–O(2)#1	2.2749(18)
Cd(1)–O(2)	2.2749(18)
Cd(1)–O(3)#2	2.2803(18)
Cd(1)–O(3)#3	2.2803(18)
Cd(1)–O(4)#1	2.317(2)
Cd(1)–O(4)	2.317(2)
Cl(1)–C(4)	1.740(3)
C(9)–O(2)	1.244(3)
C(9)–O(3)	1.256(3)
C(9)–C(8)	1.513(3)
O(1)–C(1)	1.382(3)
O(1)–C(8)	1.418(3)
O(3)–Cd(1)#4	2.2803(18)
C(1)–C(6)	1.376(4)
C(1)–C(2)	1.395(4)
C(2)–C(3)	1.392(5)
C(2)–C(7)	1.479(5)
C(6)–C(5)	1.388(4)
C(5)–C(4)	1.364(5)
C(4)–C(3)	1.371(5)
Angles	
O(2)#1–Cd(1)–O(2)	180.0
O(2)#1–Cd(1)–O(3)#2	77.51(7)
O(2)–Cd(1)–O(3)#2	102.49(7)
O(2)#1–Cd(1)–O(3)#3	102.49(7)
O(2)–Cd(1)–O(3)#3	77.51(7)
O(3)#2–Cd(1)–O(3)#3	180.0
O(2)#1–Cd(1)–O(4)#1	85.85(7)
O(2)–Cd(1)–O(4)#1	94.15(7)
O(3)#2–Cd(1)–O(4)#1	90.56(8)
O(3)#3–Cd(1)–O(4)#1	89.44(8)
O(2)#1–Cd(1)–O(4)	94.15(7)
O(2)–Cd(1)–O(4)	85.85(7)
O(3)#2–Cd(1)–O(4)	89.44(8)
O(3)#3–Cd(1)–O(4)	90.56(8)
O(4)#1–Cd(1)–O(4)	180.0
O(2)–C(9)–O(3)	125.0(2)
O(2)–C(9)–C(8)	119.3(2)
O(3)–C(9)–C(8)	115.7(2)
C(1)–O(1)–C(8)	117.6(2)
C(9)–O(2)–Cd(1)	124.90(16)
C(9)–O(3)–Cd(1)#4	135.84(16)
C(6)–C(1)–O(1)	123.5(2)
C(6)–C(1)–C(2)	121.2(3)
O(1)–C(1)–C(2)	115.3(3)
C(3)–C(2)–C(1)	117.3(3)
C(3)–C(2)–C(7)	121.8(3)
C(1)–C(2)–C(7)	120.9(3)
O(1)–C(8)–C(9)	114.6(2)
C(1)–C(6)–C(5)	120.0(3)
C(4)–C(5)–C(6)	119.4(3)
C(5)–C(4)–C(3)	120.7(3)
C(5)–C(4)–Cl(1)	119.1(3)
C(3)–C(4)–Cl(1)	120.2(3)
C(4)–C(3)–C(2)	121.3(3)
Torsion angles	
C(5)–C(6)–C(1)–O(1)	177.2(3)
C(6)–C(1)–O(1)–C(8)	−11.8(4)
C(1)–O(1)–C(8)–C(9)	85.8(3)
O(1)–C(8)–C(9)–O(3)	−179.4(2)
C(3)–C(2)–C(1)–O(1)	−177.2(3)
C(2)–C(1)–O(1)–C(8)	166.9(2)
C(1)–O(1)–C(8)–C(9)	85.8(3)
O(1)–C(8)–C(9)–O(2)	3.4(4)
C(7)–C(2)–C(1)–O(1)	1.9(4)

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

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for the complex

	x/a	y/b	z/c	$U_{(eq)}$
Cd(1)	0	5000	5000	32(1)
Cl(1)	4672(1)	2481(2)	4352(2)	102(1)
C(9)	720(1)	3780(3)	1837(3)	30(1)
O(1)	1837(1)	5285(3)	953(2)	39(1)
O(2)	830(1)	4705(3)	3127(2)	37(1)
O(3)	186(1)	2670(3)	1489(2)	45(1)
O(4)	977(1)	6369(3)	6678(3)	44(1)
C(1)	2481(2)	4580(4)	1825(3)	36(1)
C(2)	3107(2)	5737(4)	1912(4)	45(1)
C(8)	1235(2)	4040(4)	524(3)	37(1)
C(6)	2523(2)	2848(4)	2540(4)	45(1)
C(5)	3201(2)	2211(5)	3335(4)	57(1)
C(4)	3821(2)	3314(6)	3397(4)	59(1)
C(3)	3777(2)	5054(5)	2714(4)	56(1)
C(7)	3055(3)	7604(6)	1154(6)	73(1)

$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE IV Hydrogen bonds in the complex, with distances in Å and angles in deg

$D–H\cdots A$	$d(D–H)$	$d(H\cdots A)$	$d(D\cdots A)$	$<(DHA)$
O(4)–H(4O)$\cdots$O(3)#1	0.77(3)	2.13(3)	2.804(3)	147(3)
O(4)–H(4O)$\cdots$O(2)#5	0.77(3)	2.51(4)	3.091(3)	134(3)
O(4)–H(4P)$\cdots$O(1)#5	0.72(3)	2.30(4)	2.963(3)	153(4)

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

group, mainly ν_{asym}(OCO) and ν_{sym}(OCO). The criterion for distinguishing the main types of acetate binding is the magnitude of separation (Δ) between ν_{asym} and ν_{sym}. Δ values change in the order unidentate group $\gg$ bridging bidentate group $>$ chelating bidentate group [13]. For the $Cd(MCPA)_2 \cdot 2H_2O$ complex, ν_{asym}(OCO) and ν_{sym}(OCO) are 1605 and 1421 cm^{-1}, respectively, and $\Delta\nu$ is 184 cm^{-1}. This shows that the acetate group in the title compound is coordinated as a bridging bidentate group.

RESULTS AND DISCUSSION

A perspective view of the asymmetric unit of the unit cell together with the atom numbering scheme is shown in Fig. 1. The cadmium atom lies on an inversion centre (special positions *a* of space group $P2_1/c$ at 0, ½, ½ [14]). The cadmium atom is six coordinated by four oxygen atoms from two pairs of monodentate carboxyl groups connected by a twofold screw axis and two oxygen atoms of water molecules (Fig. 2). These are related by an inversion center, which means that each carboxyl group bridges two metal atoms. In this way two-dimensional, infinite polymer nets with the $Cd[(C_9H_8ClO_3)\ (H_2O)]_2$ repeat unit are formed parallel to the *yz* plane (Fig. 3) with MCPA molecules lying along the *x* axis. Each net mesh is created from sixteen atoms (four cadmiums, four carbons and eight oxygens). In most polymeric structures, the carboxylic group acts as a chelating and bridging group, and there is only one polymer of the type present

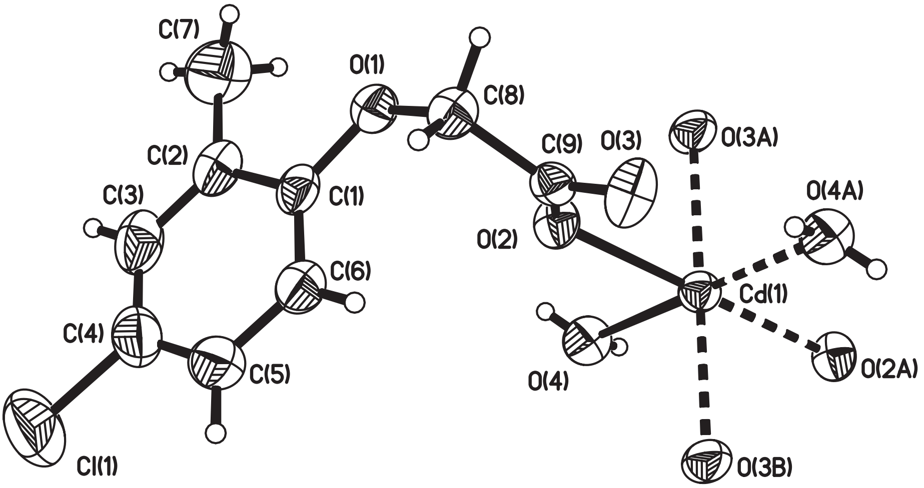

FIGURE 1 The molecular conformation of the asymmetric unit of the complex with atom numbering, plotted with 50% probability displacement ellipsoids

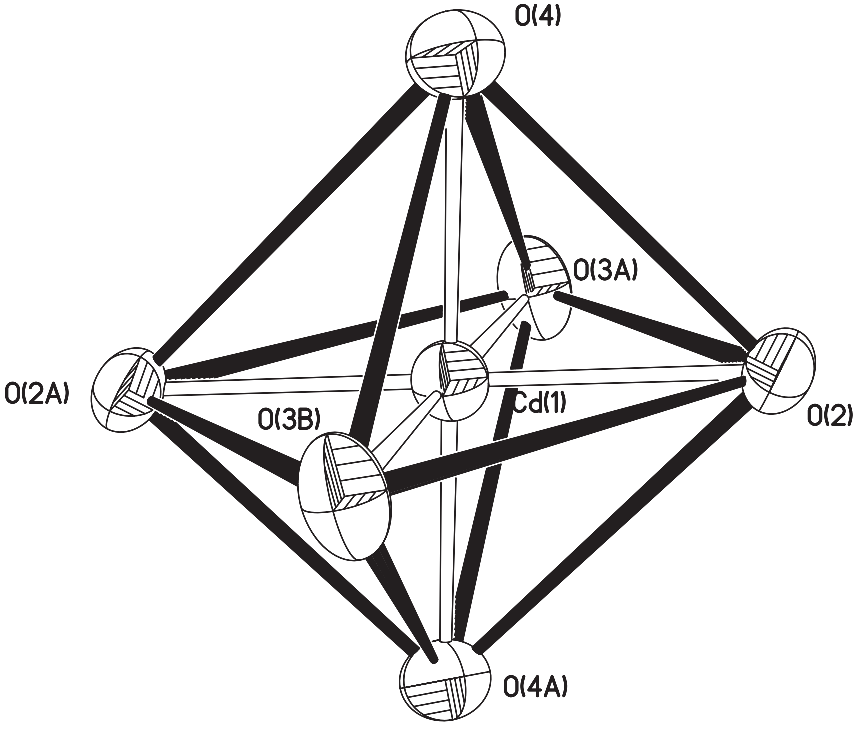

FIGURE 2 The environment around the cadmium ion

in the current work among some 77 polymeric carboxyl–cadmium structures reported in the literature [4,5]. The cadmium atom adopts almost ideal tetragonal bipyramid (4 + 2) coordination (Fig. 2). Cadmium–oxygen distances are slightly different, as found for other cadmium complexes in related structures [5], and can be compared

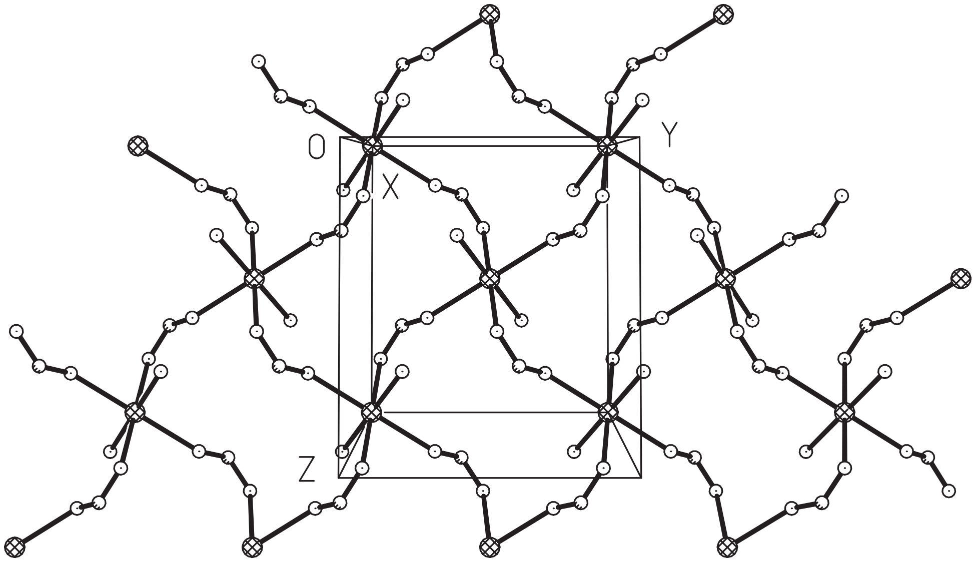

FIGURE 3 Fragment of the infinite polymer net created by sixteen-membered rings parallel to the *yz* plane. Atoms not involved in the net are omitted for clarity

to those found for lead carboxylates and those formed by a chelating acetate in nonpolymeric structures [15]. Bond valences were computed as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/B]$[16–18], where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} is the single-bond length between i and j atoms [19]). $R_{\mathrm{Cd-O}}$ was taken as being 1.904 [20] and the value of B was taken as 0.37 [16,17]. The computed bond valences of the cadmium are $\nu_{\mathrm{Cd(1)-O(2)}} = 0.367$, $\nu_{\mathrm{Cd(1)-O(3)}} = 0.362$, $\nu_{\mathrm{Cd(1)-O(4)}} = 0.328$ v.u. (valence units). It has been stated that the bond length to bond valence correlation represents a measure of the strength of a bond that is independent of the atom size [21]. Application of this correlation establishes that when both carboxylic oxygen atoms are bonded with almost the same strength, the oxygen atom of the water molecule is significantly weaker. 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 Cd(1) atom is 2.11 v.u., which is slightly larger than the formal oxidation state of the cadmium. Violation of the valence-sum rule indicates errors in the interpretation of the structure by omission or addition of weak hydrogen bonds, and can show that bonds are strained as the result of crystallographic constraints that prevent bonds from attaining their ideal lengths [19,22]. These, together with previous considerations, imply that the cadmium–carboxyl oxygen bonds are shortened by geometric constraints imposed by the rigid polymer net by about 0.3 Å.

The polymer net is stabilized via two medium strength intramolecular hydrogen bonds [23] (Table IV) linking coordinated water molecules and acetate group oxygen atoms [O(4)–H(4O)$\cdots$O(3# $-x, -y+1, -z+1$) with donor acceptor distance 2.804(3) Å, angle 147(3)°; O(4)–H(4O)$\cdots$O(2# x, $-y+3/2$, $z+1/2$), D–A 3.091(3) Å, angle 134(3)°]. In addition, a water molecule is involved in an intramolecular hydrogen bond with an oxygen atom of the phenoxy group [O(4)$\cdots$O(1# x, $-y+3/2$, $z+1/2$), distance 2.963(3) Å, O–H$\cdots$O angle 153(4)°]; this provides additional stabilization of the polymer side groups. Bond distances and angles within the MCPA molecule are comparable to those found for the free acid [24] and its complexes [25–27], but standard deviations are considerably smaller. The side-chain conformation, best illustrated by the torsion angle about the oxygen atom from the phenoxy group and an adjacent acetate carbon atom (+85.8(3)°), is comparable to that found for the manganese complex (−80.1°) [25], and quite different from that of the free MCPA molecule (+173.5°) [24]. The least-squares planes calculated through the acetate [maximum deviation −0.014(2) Å for C(9)] and the 4-chloro-2-methylphenoxy [maximum deviation −0.052(2) Å for O(1)] groups makes a dihedral angle 84.0(1)°. The benzene ring is planar within experimental error. The possibility of stacking of aromatic rings was rejected because of geometric constraints. The shortest cadmium–cadmium distance is 5.453(1) Å and there are no unusually short intermolecular contacts between polymer layers. This explains the shape of the crystals–very thin plates.

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Supplementary Data

Tables of crystal data and structure refinement details, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre, No. CCDC 166048.

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