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Poly[[μ-aqua-bis(μ-2,4-dichlorophenoxyacetato)barium(II)] monohydrate]

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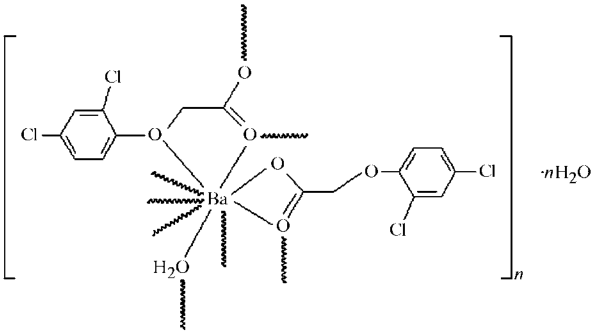
In the title coordination polymer, $\{[Ba(C_8H_5Cl_2O_3)_2(H_2O)]\cdot H_2O\}_n$, each Ba^{II} atom is nine-coordinated by six carboxylate O atoms and one ether O atom from five symmetry-related 2,4-dichlorophenoxyacetate ligands, and by two O atoms from water molecules, thus defining a distorted tricapped trigonal prism. The Ba^{II} ions are bridged by bidentate water molecules and by tridentate and tetradentate 2,4-dichlorophenoxyacetate groups, leading to a two-dimensional layer structure. The crystal structure is further stabilized by hydrogen-bonding interactions within each layer.

Comment

The formation of metal–organic coordination polymers has received much attention in recent years (Plater *et al.*, 1998). In this context, it is surprising to see the relatively small number of group II coordination polymers in the literature (Platers *et al.*, 1997). In addition, the coordination number is not limited to six for the larger Group II metals, where a higher coordination number may be expected. 2,4-Dichlorophenoxyacetic acid, which has been commonly used in herbicides and plant-growth substances (Lv, 1998), has versatile bonding modes with metal ions (Liang *et al.*, 2002) and, because of its versatile coordination modes, may take part in hydrogen-bonding interactions by functioning as either a hydrogen-bond donor or acceptor. We report here a novel two-dimensional coordination polymer, (I), based on the Group II Ba^{II} atom with the 2,4-dichlorophenoxyacetate dianion. Owing to metal–ligand interactions, the metal forms a two-dimensional layer pattern.



(I)

The structure of the title complex (Fig. 1) is built up from polymeric aquabis(2,4-dichlorophenoxyacetato)barium(II) units and solvent water molecules. Each Ba^{II} atom binds to nine O-donor atoms, seven of which belong to five symmetry-related 2,4-dichlorophenoxyacetate ligands (six carboxylate O atoms and one ether O atom) and the remaining two to two water molecules. Thus, the coordination geometry around the Ba^{II} atom is a distorted tricapped trigonal prism, in which atoms O3, O5 and O2W^{i} [symmetry code: (i) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$] form the bottom plane of the trigonal prism and the top plane is completed by atoms O2W, O5^{i} and O2^{iii} [symmetry code:

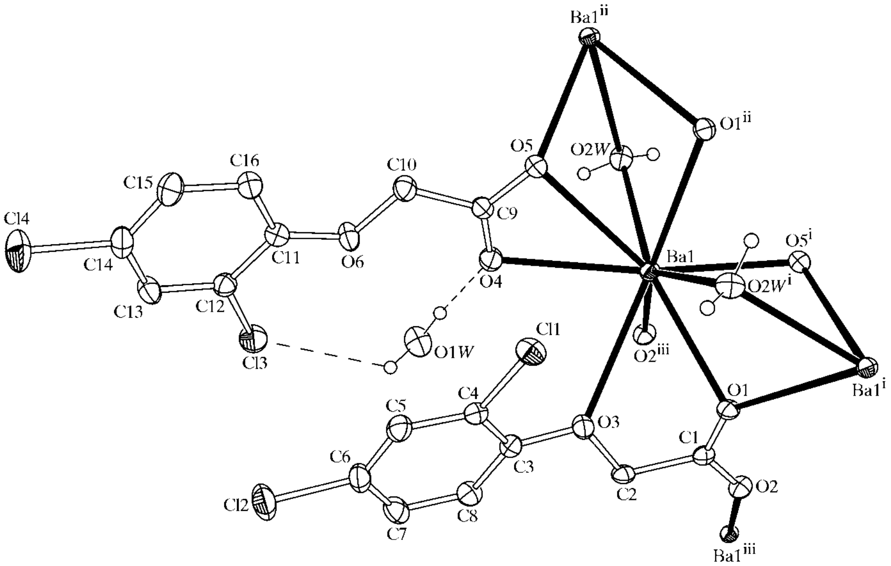


Figure 1
The molecular structure of (I), with displacement ellipsoids shown at the 30% probability level. C-bound H atoms have been omitted. [Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x, -y+2, -z+1$.]

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(iii) $-x, -y+2, -z+1$]; the dihedral angle between the planes is 0.509 (5)°. Atoms O1, O4 and O1$^{\rm ii}$ [symmetry code: (ii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$] cap each quadrilateral face of the trigonal prism (Fig. 2). The Ba—O$_{\rm carboxyl}$ bond lengths (Table 1) range from 2.720 (5) to 3.050 (5) Å, a deviation caused by the asymmetric coordination mode of the 2,4-dichlorophenoxyacetate groups. The chelating modes of the two O atoms from the same 2,4-dichlorophenoxyacetate groups also cause bond-angle deviations from idealized tricapped trigonal prisms. In each ligand, the oxyacetate group and aromatic ring are not perfectly coplanar, the torsion angles being −166.0 (5) (C3—O3—C2—C1) and 168.8 (6)° (C11—O6—C10—C9).

Fig. 3 shows the two-dimensional network of the title coordination polymer. The two types of 2,4-dichlorophenoxyacetate ligands are distinguished by two bridging modes: one adopts a tetradentate mode and the other a tridentate mode. The water molecules and 2,4-dichlorophenoxyacetate ligands are linked to Ba atoms and give one five-membered chelate ring and seven four-membered rings. In such a way, the complex units are assembled into a two-dimensional infinite layer structure parallel to the (100) plane. Within each layer there are also hydrogen bonds involving the coordinated and solvent water molecules (Table 2).

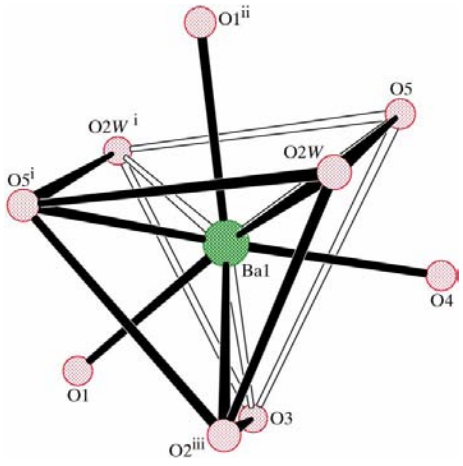

Figure 2
The coordination polyhedron of the Ba atom in (I). [Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x, -y+2, -z+1$.]

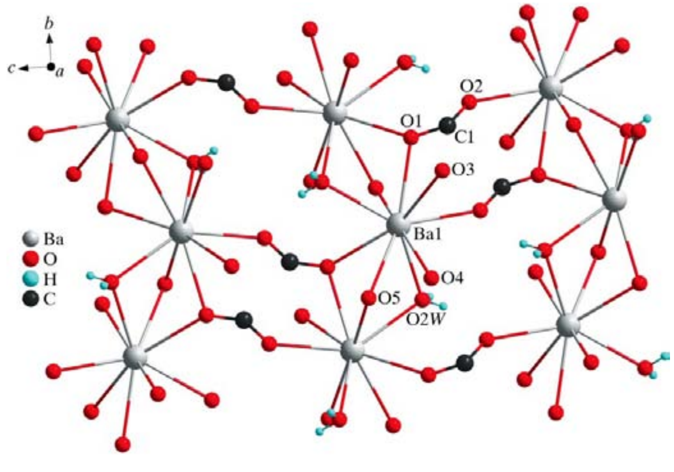

Figure 3
Part of the two-dimensional layer structure of (I), with 2,4-dichlorophenoxy aromatic rings and H atoms on C atoms omitted.

Experimental

2,4-Dichlorophenoxyacetic acid was synthesized according to a literature method (Wu *et al.*, 1996). $BaCl_2\cdot 2H_2O$ (2.40 g, 10 mmol) and 2,4-dichlorophenoxyacetic acid (4.42 g, 20 mmol) were dissolved in a 1:2 ethanol/water mixture and the pH of the solution was adjusted to 7 with 0.1 *M* sodium hydroxide. The reaction mixture was stirred for 30 min at room temperature and then filtered. Colorless crystals formed over a period of a few days in the solution left at room temperature. Analysis calculated for $C_{16}H_{14}BaCl_4O_8$: C 31.33, H 2.30%; found: C 31.29, H 2.31%.

Crystal data

$[Ba(C_8H_5Cl_2O_3)_2(H_2O)]\cdot H_2O$
$M_r = 613.41$
Monoclinic, $P2_1/c$
$a = 18.671$ (4) Å
$b = 7.7027$ (15) Å
$c = 14.002$ (3) Å
$\beta = 90.99$ (3)°
$V = 2013.4$ (7) Å^3
$Z = 4$
$D_x = 2.024$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.55$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
0.36 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\rm min} = 0.471$, $T_{\rm max} = 0.637$
14924 measured reflections
3541 independent reflections
3185 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.087$
$\theta_{\rm max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.123$
$S = 1.08$
3541 reflections
274 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0081P)^2 + 16.8794P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 2.32$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.50$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ba1—O1	2.844 (4)	Ba1—O5	2.922 (5)
Ba1—O1$^{\rm ii}$	2.863 (4)	Ba1—O5$^{\rm i}$	2.720 (5)
Ba1—O2$^{\rm iii}$	2.790 (5)	Ba1—O2W	2.845 (5)
Ba1—O3	3.050 (5)	Ba1—O2$W^{\rm i}$	2.861 (5)
Ba1—O4	2.894 (5)		

Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x, -y+2, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O4	0.85 (5)	1.86 (6)	2.699 (7)	170 (4)
O1W—H1W2···Cl3	0.85 (4)	2.70 (8)	3.296 (6)	128 (8)
O2W—H2W1···O1$W^{\rm iv}$	0.85 (4)	1.89 (3)	2.709 (7)	163 (8)
O2W—H2W2···O2$^{\rm v}$	0.85 (5)	2.00 (7)	2.824 (7)	163 (8)

Symmetry codes: (iv) $-x, -y+1, -z+1$; (v) $x, y-1, z$.

H atoms attached to C atoms were placed in calculated positions and treated as riding, with C—H distances of 0.93 and 0.97 Å, and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). H atoms of water molecules were located in a difference Fourier map and refined with an O—H distance restraint of 0.85 (1) Å and $U_{\rm iso}$(H) values of $1.5U_{\rm eq}$(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3031). Services for accessing these data are described at the back of the journal.

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