Hexaaquacobalt(II) bis[hydrogen bis(4-carboxyphenylphosphonate)] dihydrate

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The Co^{II} ion in the title complex salt, [Co(H$_2$O)$_6$](C$_{14}$H$_{13}$O$_{10}$P$_2$)$_2$·2H$_2$O or [Co(H$_2$O)$_6$][H(C$_7$H$_6$O$_5$P)$_2$]·2H$_2$O, resides on an inversion centre and exhibits an octahedral environment formed by six aqua ligands. Two unique acid residues share an H atom between their phosphonate groups, forming a complex monoanion with a very short (P)O···H···O(P) hydrogen bond of 2.435 (2) Å. The crystal structure is layered and consists of thick organic bilayers with hydrated metal [Co(H$_2$O)$_6$]$^{2+}$ ions arranged between them. The interior of the bilayer is occupied by the aromatic portions of the complex monoanions and the carboxyl groups, which form hydrogen-bonded $R_2^2(8)$ ring motifs. The phosphonate groups are arranged outwards in order to form the hydrogen-bonded surfaces of the bilayer. Electrostatic and multiple hydrogen-bond interactions, established between the coordination and solvent water molecules and the phosphonate O atoms, hold neighbouring bilayers together.

Comment

The chemistry of metal organophosphonates has attracted considerable attention for a long time, due to the potential applications of these materials as ion exchangers, catalysts, proton conductors and sensors (Clearfield, 1998; Alberti *et al.*, 1996; Cao *et al.*, 1992). Recently, consideration has been devoted to metal arylphosphonates, in which an additional functional group, especially a carboxyl group, is attached to the aromatic ring. Multifunctional acids have been found to be better ligands, since they provide additional coordination sites and allow the formation of novel complexes with variable structures and versatile properties. In particular, 4-carboxyphenylphosphonic acid has been widely used to form inorganic–organic hybrid compounds with the transition metal ions Ni^{2+} (one compound), Cu^{2+} (eight) and Zn^{2+} (16), as well as with main group metals (12) or rare earth metal ions

(three). It has also been used as a ligand in three oxovanadium– and seven oxomolybdenum–organophosphonate/ secondary metal–organonitrogen ligand systems. A literature survey revealed that the majority of the 50 metal 4-carboxyphenylphosphonate structures reported to date were studied during the last two years. The acid residues in them appear in different forms, from intact acid up to fully deprotonated trianion, and the metal ions are coordinated by O atoms from the phosphonate or from both phosphonate and carboxylate functional groups. However, to the best of our knowledge, there are no metal ion compounds of 4-carboxyphenylphosphonic acid in which both the anion and cation appear in complex form. A search of the Cambridge Structural Database (CSD, Version 5.31; Allen, 2002) returned only 24 organophosphonate crystal structures in which the H atom is shared between two neighbouring phosphonate sites in order to form a complex anionic unit *via* very short linear hydrogen bonds (O···O distances = 2.37–2.45 Å and O—H—O angles = 176–180°). In all but three of those compounds the hydrogen bond is symmetry-constrained. Here, we report the crystal structure of the title compound, (I), where there is no symmetry restriction imposed on the shared H atom.

(I)
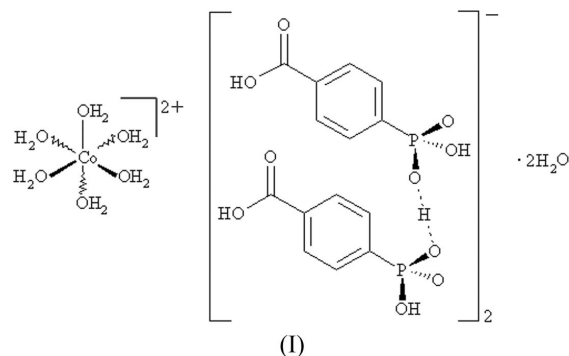
The asymmetric unit of (I) contains half a Co^{II} ion, two acid residues and four symmetry-independent water molecules (Fig. 1). The metal ion is six-coordinate with a slightly distorted octahedral geometry, and occupies a special position on the inversion centre at $(\frac{1}{2}, \frac{1}{2}, 0)$. Six water molecules, three of which are unique, fill the first coordination sphere of the Co^{II} ion in order to form the [Co(H$_2$O)$_6$]$^{2+}$ unit. Atoms O2W, O2W^i, O3W and O3W^i (symmetry code as in Table 2) act as equatorial ligands and create two pairs of similar bonds (Co1—O2W and Co1—O3W), whereas the axial ligands O1W and O1W^i form a somewhat longer bond (Co1—O1W) (Table 1).

The bond distances and angles observed in both acid residues are within the usual ranges for carboxyl [1.226 (20) and 1.305 (20) Å] and phosphonic groups [1.457 (9) and 1.571 (13) Å] (Allen *et al.*, 1987), although the P11—O12 and P21—O22 bond distances are intermediate between single and double P—O bonds. This reflects the migration of the H atom from the formal phosphonic acid group to the phosphonate group of an adjacent residue, in order to form a complex [H(HO$_3$PC$_6$H$_4$COOH)$_2$]$^−$ monoanion *via* a very short (P)O22···H22O···O12(P) hydrogen bond (Fig. 1). Despite the very short distance of 2.435 (2) Å between the O-atom
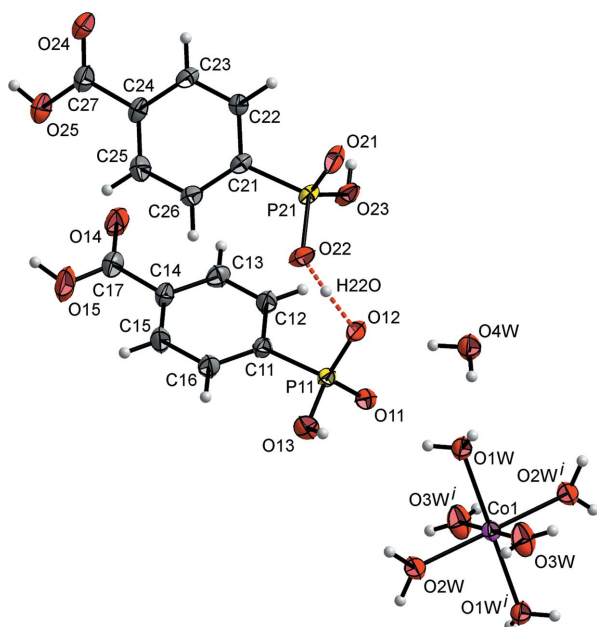
metal-organic compounds

Figure 1
The asymmetric unit of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates the short hydrogen bond between the two phosphonate portions of the complex monoanion. [Symmetry code: (i) $-x + 1, -y + 1, -z$.]

sites in the dimeric unit, the position of atom H22O is not confined by any symmetry elements and its environment is asymmetric. The hydrogen bond is almost linear, but the two O—H distances are somewhat different (Table 2). The acid residues on either side of the hydrogen bond are symmetry-unique and one of the carboxyl groups is rotated by 11.45 (12)° relative to the plane of the benzene ring to which it is bonded, whereas the second group is almost coplanar with the corresponding ring. The acid dimers are organized into a polar monolayer with the help of two other hydrogen bonds, *viz.* O13—H13O···O21^{iii} and O23—H23O···O11^{vi} (symmetry codes as in Table 2), established between the different phosphonate sites. The (P)O—H···O(P) hydrogen-bonded network is two-dimensional, parallel to the crystallographic *bc* plane, and is characterized by large $R_6^6(24)$ motifs (Bernstein *et al.*, 1995) which are arranged in a herringbone fashion (Fig. 2*a*). The aromatic rings of the monoanions are arranged on one side of the monolayer. The 4-carboxyl groups connect neighbouring inversion-related monolayers *via* two different carboxyl–carboxyl hydrogen-bond interactions, *viz.* O15—H15O···O24^v and O25—H25O···O14^{vii} (symmetry codes as in Table 2), in order to form a thick organic bilayer. The phosphonate sites of the complex monoanion create the outer surfaces of the bilayer, while the aromatic rings and the $R_2^2(8)$ synthons form its interior (Fig. 2*b*).

The [Co(H$_2$O)$_6$]$^{2+}$ units are arranged between the anionic bilayers. The aqua ligands serve both to complete the coordination environment of the Co^{II} ion and to crosslink the bilayers *via* water–phosphonate hydrogen bonds in order to construct the three-dimensional crystal structure. However, each hydrated Co^{II} ion is surrounded by six phosphonate

groups from two neighbouring bilayers. Five different hydrogen bonds are formed between the water molecules of the first coordination sphere and the phosphonate O atoms of the second (Fig. 3*b*). Four of these, *viz.* O2W—H1W2···O11^{iv},
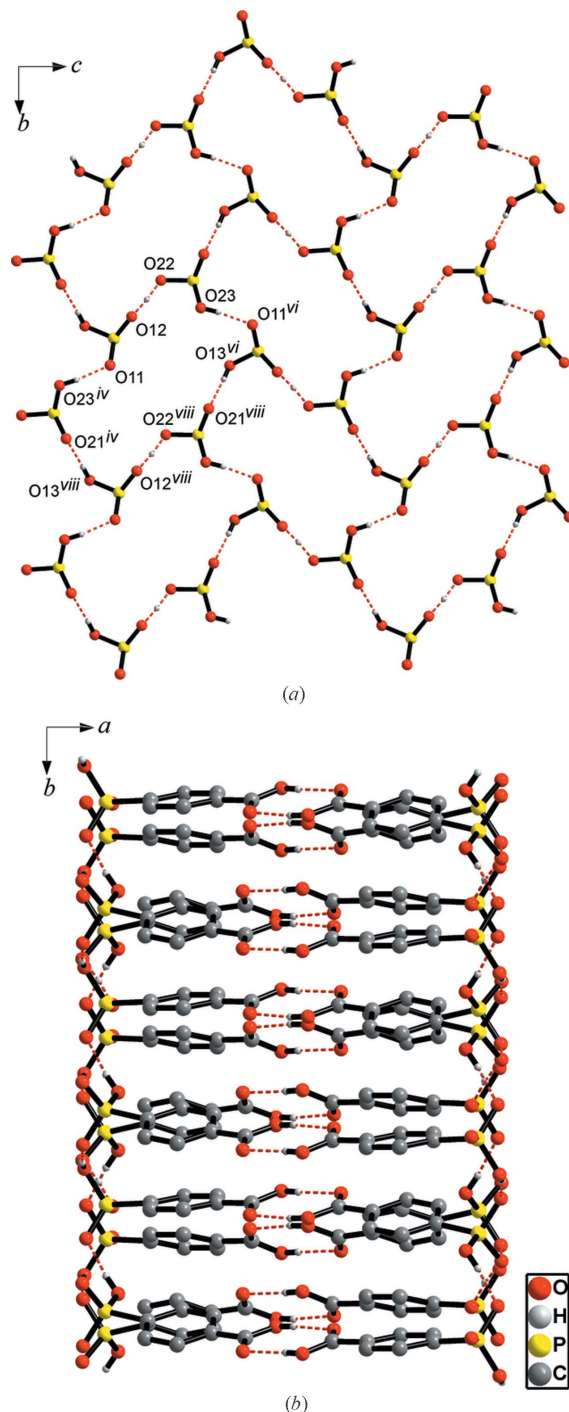

(*a*)

(*b*)

Figure 2
(*a*) The two-dimensional hydrogen-bonded network formed between the phosphonate sites of the hydrogen bis(4-carboxyphenylphosphonate) monoanions on the surface of the bilayer. Aromatic rings and carboxyl groups have been omitted for clarity. (*b*) The arrangement of the aromatic rings and carboxyl groups in the interior of the bilayer. The H atoms of the aromatic rings have been omitted for clarity. [Symmetry codes: (iv) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (vi) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (viii) $x, y + 1, z$.]
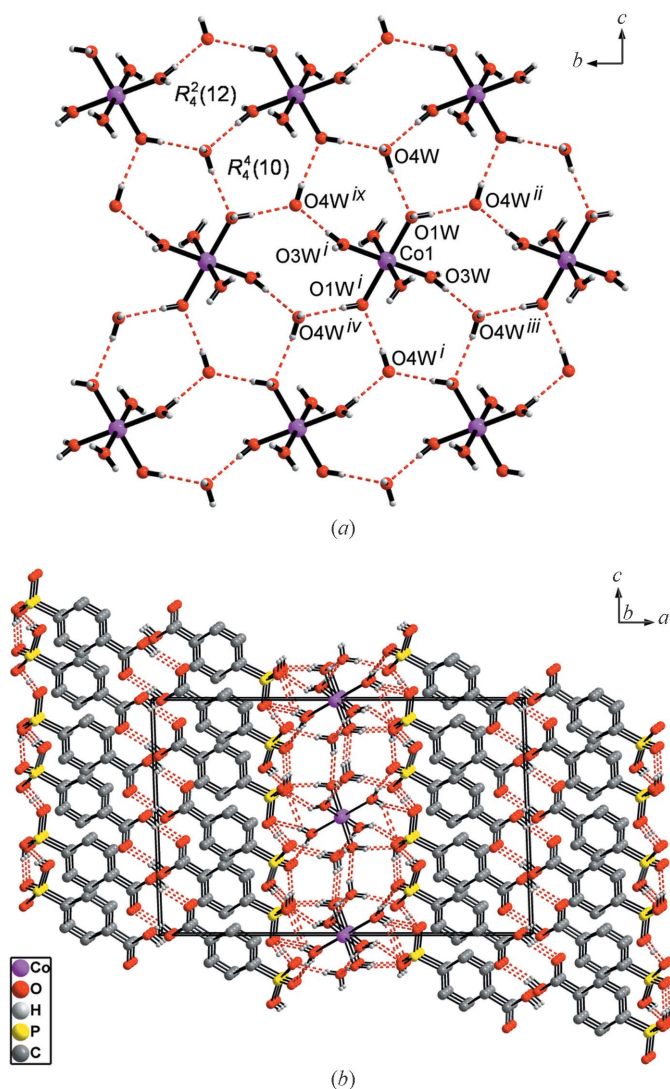
Figure 3
(a) A view of the two-dimensional hydrogen-bonded network established between the $[Co(H_2O)_6]^{2+}$ cationic units and the solvent water molecules. (b) The three-dimensional packing arrangement of (I), viewed along the b axis. [Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ix) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.]

$O2W—H2W2\cdots O21^{iii}$, $O2W—H2W2\cdots O22^{iii}$ and $O3W—H2W3\cdots O23^{ii}$, are donated from the equatorial ligands, and the fifth, $O1W—H2W1\cdots O21^{iii}$, from the axial ligands. The small channels generated along the b axis are occupied by the O4W solvent water molecules, which serve both to fill the empty spaces of the structure and to connect the coordination units into a two-dimensional network. There are six O4W solvent water molecules around the $[Co(H_2O)_6]^{2+}$ unit, and each of them is used to mediate three cationic units via three different hydrogen bonds from or to the aqua ligands, viz. $O1W—H1W1\cdots O4W^{ii}$, $O3W—H2W3\cdots O4W^{iii}$ and $O4W—H2W4\cdots O1W$. Two types of water ring motifs, $R_4^4(10)$ and $R_4^2(12)$, are formed around the Co^{II} ions, which tessellate in order to produce a two-dimensional hydrogen-bonded network of Co^{II} ions (Fig. 3a). An additional $O4W—H1W4\cdots O12$ bond is established between the solvent water and the organic monolayer.

In conclusion, the title compound, (I), demonstrates a layered structure with thick organic bilayers and inorganic monolayers, which crosslink the bilayers via multiple hydrogen bonds. De facto, the crystal packing of the compound generates hydrophobic and hydrophilic regions that alternate along the crystallographic a axis. However, the hydrophilic regions, arranged on both sides of the aromatic region, are different: one of them contains hydrogen-bonded $R_2^2(8)$ ring motifs formed by the carboxyl groups of the monoanions, and the other consists of the phosphonate groups and hydrated metal ions (Fig. 3b). In this view, the structure of (I) resembles the packing patterns of some other metal 4-carboxyphenylphosphonate compounds with divalent metal ions like calcium (Svoboda et al., 2005), strontium (Zima et al., 2007), barium (Svoboda et al., 2008) and copper(II) ions (Li et al., 2008; Zima et al., 2009). The major structural difference observed in these structures is a direct metal–phosphonate contact via $M—O$ bonds, making the inorganic monolayer more compact.

Experimental

All chemicals were obtained commercially, with the exception of 4-carboxyphenylphosphonic acid, which was prepared according to the published procedure of Hirao et al. (1981). The title compound was synthesized by mixing 4-carboxyphenylphosphonic acid (30 mg, 0.15 mmol) dissolved in diethylamine (20 µl) and ethanol (1 ml) with cobalt(II) chloride (19 mg, 0.15 mmol) dissolved in ethanol (0.5 ml). A navy-blue solution was obtained and this was kept at room temperature to allow slow evaporation of the solvent. After one week, pink parallelepiped crystals of (I) of sufficient quality for X-ray diffraction measurements were obtained.

Spectroscopic analysis, FT–IR (KBr, cm^{-1}). Internal vibrations of the functional groups: $\nu C{=}O$ 1687 (vs), 1628 (sh); $\delta(C)O—H$ and $\nu C—OH$ 1427 (s), 1400 (m), 1375 (m), 1323 (s); νPO_3 1172 (s, sh), 1143 (vs), 1115 (vs), 1090 (m, sh), 1029 (vs), 1013 (vs). PO_3 deformation vibrations: 580 (s, n), 546 (s, n), 518 (s, n), 460 (s, n), 448 (s, n). νOH of the hydrogen bonds: strong absorption in the region 3600–1800 cm^{-1}, with maxima at 3530 (s, b), 3408 (b, vs), 3095 (vb, vs), 2995 (vb, vs), 2895 (vb, vs), 2840 (vb, vs), 2676 (s, b), 2560 (s, b). Internal vibrations of the aromatic ring: $\nu C—C$ 1560 (m, n), 1503 (vw), 1471 (vw). Out-of-plane ring deformations: 862 (m, n), 819 (w), 805 (w), 632 (w). Ring torsions 767 (m), 719 (n, vs), 646 (s, n).

Crystal data

$[Co(H_2O)_6](C_{14}H_{13}O_{10}P_2)_2\cdot 2H_2O$	$Z = 2$
$M_r = 1009.43$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	$\mu = 0.68$ mm^{-1}
$a = 21.053$ (4) Å	$T = 295$ K
$b = 7.2030$ (14) Å	$0.36 \times 0.22 \times 0.17$ mm
$c = 13.370$ (3) Å	
$\beta = 92.00$ (1)°	
$V = 2026.3$ (7) Å^3	

Data collection

Kuma KM-4 diffractometer with a CCD area detector	26924 measured reflections
Absorption correction: numerical (CrysAlis RED; Oxford Diffraction, 2006)	5087 independent reflections
	3294 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.052$
$T_{min} = 0.843$, $T_{max} = 0.899$	

metal-organic compounds

Table 1
Selected bond lengths (Å).

Co1—O2W	2.0722 (15)	P11—O13	1.5398 (14)
Co1—O3W	2.0828 (15)	P21—O21	1.4975 (13)
Co1—O1W	2.1012 (14)	P21—O22	1.5107 (13)
P11—O11	1.4988 (13)	P21—O23	1.5394 (14)
P11—O12	1.5225 (13)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O4W^i	0.81 (2)	1.94 (2)	2.752 (2)	174 (2)
O1W—H2W1···O21^{ii}	0.79 (2)	1.86 (2)	2.644 (2)	172 (2)
O2W—H1W2···O11^{iii}	0.91 (2)	1.75 (2)	2.654 (2)	174 (2)
O2W—H2W2···O22^{ii}	0.77 (2)	2.31 (2)	3.060 (2)	168 (3)
O2W—H2W2···O21^{ii}	0.77 (2)	2.62 (2)	3.178 (2)	131 (2)
O3W—H1W3···O4W^{ii}	0.80 (3)	1.96 (3)	2.758 (2)	179 (3)
O3W—H2W3···O23^i	0.78 (3)	2.33 (3)	2.972 (2)	141 (2)
O4W—H1W4···O12	0.86 (2)	1.90 (2)	2.761 (2)	172 (2)
O4W—H2W4···O1W	0.80 (2)	2.10 (2)	2.886 (2)	169 (2)
O22—H22O···O12	1.14 (2)	1.30 (2)	2.435 (2)	176 (2)
O13—H13O···O21^{ii}	0.84 (2)	1.68 (2)	2.523 (2)	174 (2)
O15—H15O···O24^{iv}	0.89 (3)	1.69 (3)	2.578 (2)	173 (3)
O23—H23O···O11^v	0.80 (2)	1.73 (2)	2.528 (2)	171 (2)
O25—H25O···O14^{vi}	0.84 (3)	1.82 (3)	2.658 (2)	171 (3)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of
$wR(F^2) = 0.073$	independent and constrained
$S = 1.00$	refinement
5087 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
316 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}

Difference Fourier map plots showed a prolate shaped peak between O12 and O22 and while a two H-atom disorder model for this site was considered it was decided that nothing significant would obtained by doing so; the maximum was labelled as H22O and assigned unit occupancy. That position and those of the other H atoms bonded to O atoms, also located from difference Fourier maps, were refined with U_{iso}(H) = 1.5U_{eq}(O). The H atoms of the aromatic rings were located in geometric positions and refined as rigid, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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