Cadmium bis[dihydrogenphosphate(I)]

Dmitry Yu. Naumov, Marina I. Naumova and Natalia V. Kuratieva*

Nikolaev Institute of Inorganic Chemistry, SB Russian Academy of Sciences, Akad. Lavrentiev prospekt 3, Novosibirsk 90, 630090, Russian Federation

Correspondence e-mail: kuratieva@ngs.ru

The structure of monoclinic ($C2/c$) cadmium bis[dihydrogenphosphate(I)], [Cd(H$_2$PO$_2$)$_2$], consists of layers located at $x = 0$ and $\frac{1}{2}$. The Cd cation has a distorted octahedral coordination and dihydrogenphosphate(I) anions act as tridentate bridging ligands. The Cd atoms are on sites of twofold symmetry, while all other atoms are in general positions. The compound is isotypic with Ca(H$_2$PO$_2$)$_2$ [Goedkoop & Loopstra (1959). *Ned. Tijdschr. Natuurkd.* **25**, 29–41].

Comment

Cadmium bis[dihydrogenphosphate(I)], (I), is isotypic with Ca(H$_2$PO$_2$)$_2$ (Goedkoop & Loopstra, 1959). The structure consists of layers located at $x = 0$ and $\frac{1}{2}$ (Fig. 1). The structure of one layer is shown in Fig. 2. The metal cations form distorted hexagonal grids with a shift of centers by 0.897 (1) Å along the b axis. The distance between the nearest planes through the Cd atoms is 7.399 (2) Å. Adjacent layers are linked by van der Waals interactions with shortest H···H contacts of 2.24 (10) and 2.59 (10) Å. The metal cation environment consist of six O atoms of different H$_2$PO$_2^-$ anions that are crystallographically related in pairs by a twofold rotation axis. The O atoms of the anion play different functional roles:
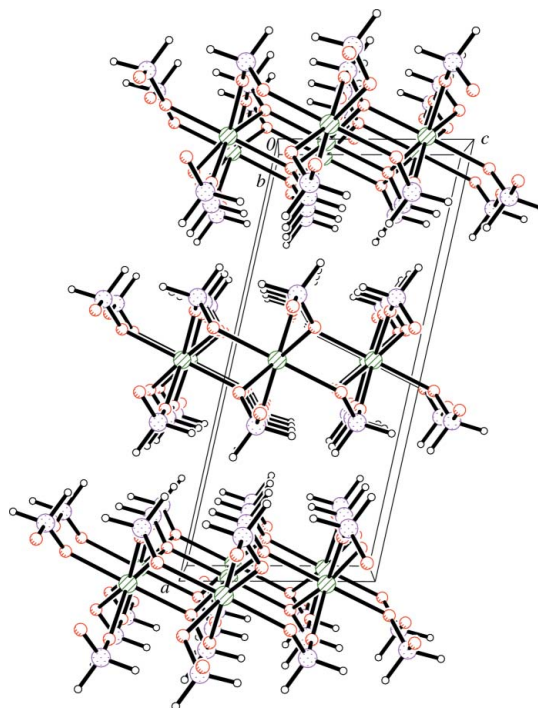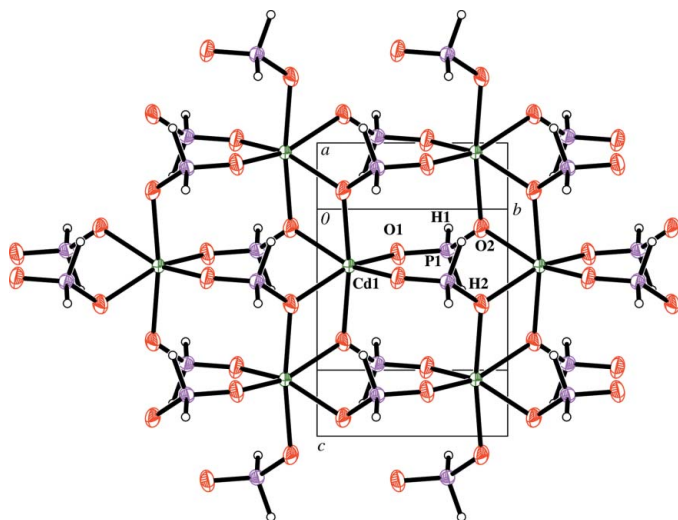

Figure 1

The crystal structure of (I), viewed along [010]. Atom colour code: Cd green hatched spheres, P pink dotted spheres, O red hatched spheres, H black plain spheres.

Figure 2
The layer formed by the Cd cations and dihydrogenphosphate(I) anions in (I), projected on to the (100) plane. Displacement ellipsoids are drawn at the 50% probability level, with H atoms shown as small spheres of arbitrary radii.

atom O1 acts as a monodentate ligand, whereas O2 is a bidentate bridging ligand, so that the entire $H_2PO_2^-$ anion exists as a tridentate ligand. The metal cation has a distorted octahedral coordination. The equatorial O atoms are displaced about 0.46 (1) Å [0.46 (2) Å in $Ca(H_2PO_2)_2$] from the average plane. Despite the different location and orientation of the anion, the Cd—O2 distances are close to each other and exceed the Cd—O1 distance by about 0.1 Å. The average Cd—O distance of 2.29 (5) Å (Table 1) is slightly shorter than that of 2.37 (5) Å in the isotypic $Ca(H_2PO_2)_2$ (Goedkoop & Loopstra, 1959).

Experimental

Compound (I) was synthesized by adding hypophosphorous acid, H_3PO_2 (1.531 g of a 50% solution in 10 ml of water), to cadmium carbonate, $CdCO_3$ (1 g). The reacting mixture was evacuated until carbon dioxide evolution had stopped (about 10 min). Single rhombic plate-like crystals were grown at 293 K from an aqueous solution within 2 d.

Crystal data

$[Cd(H_2PO_2)_2]$	$D_x = 3.036$ Mg m^{-3}
$M_r = 242.37$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 22
$a = 15.156$ (2) Å	reflections
$b = 5.4692$ (8) Å	$\theta = 9.4$–15.0°
$c = 6.5516$ (13) Å	$\mu = 4.63$ mm^{-1}
$\beta = 102.487$ (14)°	$T = 293$ (2) K
$V = 530.22$ (16) Å^3	Plate, colorless
$Z = 4$	$0.35 \times 0.17 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.017$
	$\theta_{max} = 29.9°$
$2\theta/\omega$ scans	$h = -21 \rightarrow 20$
Absorption correction: ψ scan	$k = 0 \rightarrow 7$
(*CADDAT*; Enraf–Nonius, 1989)	$l = 0 \rightarrow 9$
$T_{min} = 0.294$, $T_{max} = 0.802$	3 standard reflections
831 measured reflections	frequency: 60 min
765 independent reflections	intensity decay: none
677 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.10$	$\Delta\rho_{max} = 1.29$ e Å^{-3}
765 reflections	$\Delta\rho_{min} = -1.30$ e Å^{-3}
40 parameters	Extinction correction: *SHELXL97*
Only H-atom coordinates refined	Extinction coefficient: 0.0051 (10)

Table 1
Selected geometric parameters (Å, °).

Cd—O1	2.223 (4)	P—O2	1.510 (4)
Cd—O2^i	2.311 (4)	P—H1	1.30 (7)
Cd—O2^{ii}	2.334 (4)	P—H2	1.38 (7)
P—O1	1.484 (4)		
O1—Cd—O1^{iii}	102.0 (2)	O2^{ii}—Cd—O2^{iv}	171.93 (19)
O1—Cd—O2^i	90.03 (16)	O1—P—O2	118.3 (2)
O1—Cd—O2^{iv}	84.80 (16)	O1—P—H1	114 (3)
O1—Cd—O2^{ii}	100.32 (16)	O2—P—H1	105 (3)
O1—Cd—O2^v	155.58 (16)	O1—P—H2	107 (3)
O2^i—Cd—O2^{ii}	72.08 (16)	O2—P—H2	98 (3)
O2^i—Cd—O2^v	87.2 (2)	H1—P—H2	114 (4)
O2^v—Cd—O2^{ii}	101.88 (14)		

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

The H atoms were located in a difference electron density map and their positions were refined without any constraints (Table 1). The $U_{eq}(H)$ values were defined as 1.2 times U_{eq} of the P atom. The highest electron density peak and deepest hole are located 0.95 and 1.07 Å, respectively, from the Cd atom.

Data collection: *CD4CA0* (Enraf–Nonius, 1989); cell refinement: *CD4CA0*; data reduction: *CADDAT* (Enraf–Nonius, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

References

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