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The Crystal Structure of Cadmium Dihydrogenphosphite Monohydrate

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$\text{Cd}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$ is triclinic, space group $P\bar{1}$, with $a = 6.772$ (2), $b = 7.523$ (4), $c = 7.982$ (3) Å, $\alpha = 113.70$ (4), $\beta = 110.69$ (3), $\gamma = 95.26$ (4)°, $Z = 2$. The structure was refined to $R = 0.033$ for 1186 counter reflections. It contains two distorted octahedra, connected on one edge, with central Cd atoms [Cd—O 2.263 (3) to 2.351 (3) Å], and two phosphite anions connected by a hydrogen bond [P—O 1.494 (3) to 1.569 (3) Å, O—H...O 1.09 (6), 1.58 (7) Å, 173 (6)°].

Introduction

The study of the title compound was undertaken as part of an investigation of $\text{H}_3\text{PO}_3\text{—}M(\text{H}_2\text{PO}_3)_2\text{—H}_2\text{O}$ systems. The Cd compound was selected because it was assumed to contain a polyorthophosphite anion (Ebert & Čípera, 1966), which has not yet been studied structurally.

Experimental

The sample was prepared by reaction of phosphorous acid with cadmium phosphite under conditions following from the solubility diagram of the $\text{H}_3\text{PO}_3\text{—CdHPO}_3\text{—H}_2\text{O}$ system at 25°C (Eysseltová, 1975). The cell dimensions were determined by least squares from 15 reflection angles measured on an automatic

Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation, graphite monochromator). Intensities were collected from a $0.3 \times 0.22 \times 0.55$ mm crystal for θ between 0 and 25° . The density, $D_M = 2.89$ g cm $^{-3}$, was determined by flotation in a mixture of CH_2I_2 and CCl_4 ; $D_X = 2.90$ g cm $^{-3}$. Space group $P\bar{1}$ was assumed (Donohue, 1971). Only Lorentz-polarization corrections were applied ($\mu = 37$ cm $^{-1}$).

Table 1. Atomic coordinates ($\times 10^4$; for H $\times 10^2$) with e.s.d.'s in parentheses

	x	y	z
Cd	4240.4 (4)	2319.5 (3)	1211.7 (4)
P(1)	3105 (2)	2486 (2)	6625 (2)
P(2)	8888 (2)	2456 (2)	337 (2)
O(1)	918 (5)	2379 (5)	4964 (5)
O(2)	4913 (5)	4270 (5)	7313 (5)
O(3)	2483 (5)	2318 (5)	8207 (5)
O(4)	6934 (5)	1216 (5)	259 (5)
O(5)	1101 (4)	2454 (5)	1711 (4)
O(6)	8679 (5)	1746 (5)	8144 (5)
O(7)	6464 (6)	2712 (5)	4317 (5)
H(1)	80 (1)	30 (1)	46 (1)
H(2)	62 (1)	35 (1)	55 (1)
H(3)	2 (1)	15 (1)	82 (1)
H(4)	10 (1)	23 (1)	36 (1)
H(5)	36 (1)	8 (1)	57 (1)
H(6)	88 (1)	44 (1)	10 (1)

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses

Symmetry code

(i)	$1-x, 1-y, 1-z$	(v)	$1+x, y, z$
(ii)	$1-x, \bar{y}, \bar{z}$	(vi)	$1+x, y, z-1$
(iii)	$x, y, z-1$	(vii)	$x-1, y, z-1$
(iv)	$x-1, y, z$	(viii)	$1-x, \bar{y}, 1-z$

Cd—Cd ⁽ⁱⁱ⁾	3.690 (1)	O(1)—P(1)—O(2)	111.6 (2)
—O(4)	2.312 (4)	O(1)—P(1)—O(3)	105.3 (2)
—O(4 ⁱⁱ)	2.351 (3)	O(1)—P(1)—H(5)	104 (3)
—O(5)	2.301 (3)	O(2)—P(1)—O(3)	117.5 (2)
—O(2 ⁱ)	2.263 (3)	O(2)—P(1)—H(5)	109 (3)
—O(3 ⁱⁱⁱ)	2.269 (4)	O(3)—P(1)—H(5)	108 (3)
—O(7)	2.278 (4)		
P(1)—O(1)	1.569 (3)	O(6 ⁱⁱⁱ)—P(2)—O(4)	109.1 (2)
—O(2)	1.494 (3)	O(6 ⁱⁱⁱ)—P(2)—O(5 ^v)	110.9 (2)
—O(3)	1.511 (3)	O(6 ⁱⁱⁱ)—P(2)—H(6)	105 (3)
—H(5)	1.33 (6)	O(4)—P(2)—O(5 ^v)	114.9 (2)
P(2)—O(4)	1.515 (3)	O(4)—P(2)—H(6)	109 (3)
—O(5 ^v)	1.513 (3)	O(5 ^v)—P(2)—H(6)	107 (3)
—O(6 ⁱⁱⁱ)	1.558 (3)		
—H(6)	1.36 (6)	P(1)—O(1)—H(4)	116 (3)
O(1)—O(5)	2.665 (5)	P(2)—O(6 ⁱⁱⁱ)—H(3 ^{vi})	106 (3)
—H(4)	1.09 (6)		
O(5)—H(4)	1.58 (7)	O(1)—H(4)—O(5)	173 (6)
O(6 ⁱⁱⁱ)—H(3 ^{vi})	1.05 (7)	O(2)—H(2)—O(7)	162 (6)
O(7)—H(1)	0.97 (7)		
—H(2)	0.98 (7)	H(1)—O(7)—H(2)	112 (6)
H(1)—H(2)	1.58 (9)		
O(2)—O(7)	2.818 (5)		
O(2)—H(2)	1.87 (6)		

Structure determination

The positions of the Cd atoms were obtained from a Patterson synthesis. The remaining non-H atoms were located by Fourier synthesis and refined by least squares to an R ($= \sum |F_o| - |F_c| / \sum |F_o|$) of 0.049 with isotropic temperature factors. In further cycles, anisotropic temperature factors were refined to $R = 0.036$. The refinement was continued until the changes in the parameters were < 0.3 of their e.s.d. The positions of all H atoms were obtained from a difference synthesis. They were assigned the anisotropic temperature factors of the atoms to which they are bound. After refinement of the positions of all atoms, R attained a value of 0.033 and R_w ($= [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$) = 0.049, with the individual weights $w = 1/\sigma^2$. In the final cycles, 26 reflections which did not meet the condition $0.75 < |F_c|/|F_o| < 1.5$ were excluded. A

Table 3. Raman and IR spectra of $\text{Cd}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$

The 13 most intense lines, with intensity, I , 4–1, are shown; the precision of the determination of band position is $1\text{--}2$ cm $^{-1}$; the values are averages of four to five spectra.

Raman		IR	
I	$\tilde{\nu}$ (cm $^{-1}$)	$\tilde{\nu}$ (cm $^{-1}$)	I
3	462	464	2
3	501	501	2
1	560	556	3
		723	3
2	913	917	4
4	953	957	4
		995	4
3	1006		
		1012	3
4	1048	1050	4
3	1073		
		1080	4
		1260	3

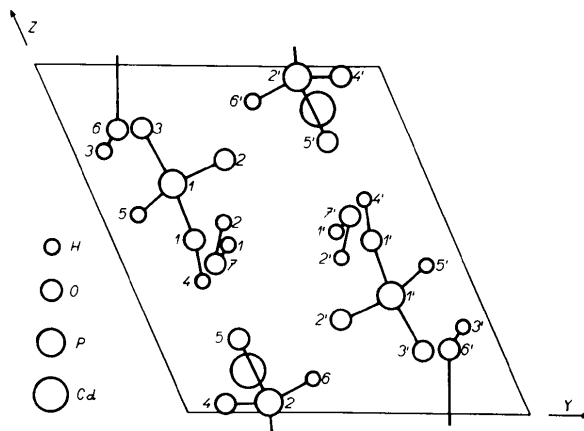


Fig. 1. Schematic projection of the structure along a .

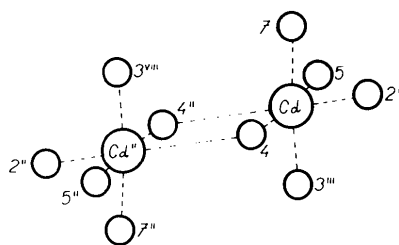


Fig. 2. Schematic representation of $(O)_4-Cd-(O)_2-Cd-(O)_4$.

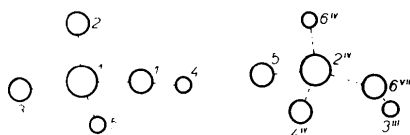


Fig. 3. Schematic representation of the bis(dihydrogenphosphite) formation.

final difference map showed no significant residual electron density.

The scattering factors for neutral non-H atoms were taken from Cromer & Waber (1965), for H from *International Tables for X-ray Crystallography* (1974). The Patterson and electron density maps were computed with *FOURIER* (Weiss, 1973), the full-matrix least-squares refinement with *ORFLS* (Busing, Martin & Levy, 1962) and interatomic distances and bond angles with *ORFFE* (Busing, Martin & Levy, 1964) on an IBM 370/135 computer.

Results and discussion

Final atomic parameters are given in Table 1.* The interatomic distances, bond angles and the symmetry code are given in Table 2. In the structure (Fig. 1) there are two interesting formations. One is composed of two distorted octahedra of O atoms connected at one edge, with central Cd atoms (Fig. 2); the other consists of two dihydrogenphosphite anions connected by a medium-strong hydrogen bond (Fig. 3). The average Cd—O(non-bridge) distance and Cd—O(bridge) are 2.278 and 2.331 Å respectively; the Cd—O(water) distance is 2.278 Å. The O—Cd—O angles are, except for two, in the range 85.6–97.0°, with an average of 89.7°. The angles $O(4)-Cd-O(4^{ii}) = 75.4^\circ$, where O(4), O(4ⁱⁱ) are bridge O atoms, and O(4)—Cd—

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32927 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

$O(2^i) = 110.0^\circ$ are exceptional. Average distances for Cd—O or Cd—O(water) agree with those in $Cd_3(P_3O_9)_2 \cdot 10H_2O$, 2.280 and 2.286 Å (Averbuch-Pouchot, Durif & Guitel, 1976) or in $CdK_2P_2O_7$, 2.290 Å (Faggiani & Calvo, 1976). The P—O and P—H distances also agree with literature data, e.g. for $Cu(H_2PO_3)_2$ (Handlovič, 1972) or LiH_2PO_3 (Philippot & Lindqvist, 1970; Johansson & Lindqvist, 1976). Two phosphite anions, e.g. with P(1) and P(2^{iv}), are always connected by a medium-strong hydrogen bond: $O(1)-H(4) \cdots O(5)$ 1.09 (6), 1.58 (7) Å, 173 (6)°. Because of this bond, these two hydrogenphosphite anions can be considered as one diorthophosphite anion $H_4P_2O_6^{2-}$ (Ebert & Čipera, 1966). Another weak hydrogen bond lies between the O atom of the phosphite anion and the water O atom, $O(2) \cdots H(2)-O(7)$ 1.87 (6), 0.98 (7) Å, 162 (6)°.

In parallel with calculations for $P\bar{I}$, calculations for $P1$ were carried out. The final atom positions in $P1$ differed from those in $P\bar{I}$ by <3 e.s.d.'s. The temperature factors in $P1$ were positive definite. As can be seen from Table 3, $P1$ and $P\bar{I}$ cannot be distinguished even by comparison of the Raman and IR spectra. The rule of mutual exclusion holds for $P\bar{I}$, i.e. vibrations active in the IR are inactive in the Raman spectrum and vice versa.

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