

## SHORT STRUCTURAL PAPERS

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*Acta Cryst.* (1982), B38, 2436–2438

## Cobalt(II) Sodium Dihydrogenphosphite Monohydrate

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(Received 1 November 1981; accepted 29 March 1982)

**Abstract.**  $\text{CoNa}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$ ,  $M_r = 342.88$ , orthorhombic,  $Pbca$ ,  $a = 9.054$  (2),  $b = 14.706$  (3),  $c = 14.759$  (3) Å,  $V = 1965.1$  (7) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.32$ ,  $D_m = 2.30$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 2.38$  mm<sup>-1</sup>;  $R = 0.046$  ( $R_w = 0.072$ ) for 1980 observed counter reflections. The structure contains three crystallographically non-equivalent  $\text{HPO}_3$  tetrahedra. The hydrogen bonds give rise to a three-dimensional network in which the Co and Na atoms are surrounded by octahedra of O atoms.

**Introduction.** The compound  $\text{CoH}_7\text{P}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  was prepared under the conditions following from the solubility diagram of the  $\text{H}_3\text{PO}_3\text{--CoHPO}_3\text{--H}_2\text{O}$  system at 298 K (Ebert & Eysseltová, 1968). From a material remaining after the investigation, well-developed crystals were formed after several years. Chemical analysis indicated that the material was contaminated by Na and corresponded to the formula  $\text{CoNa}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$ . In view of the fact that no structural data are available for double hydrogenphosphites, a crystal-structure determination of the title compound was carried out.

Weissenberg photographs showed systematic absences ( $0kl: k = 2n + 1, h0l: l = 2n + 1, hk0: h = 2n + 1$ ) indicating the space group  $Pbca$ . A crystal ground to obtain a spherical shape ( $r = 0.35$  mm) was mounted on a Hilger & Watts four-circle diffractometer. Mo  $K\alpha$  radiation was used. Cell dimensions were refined from the setting angles of 24 reflections. 2142 independent reflections with  $2\theta \leq 54^\circ$  were measured by the  $\omega$ - $2\theta$  scanning technique. The scan speed varied from 1 to 4°

min<sup>-1</sup>. The scanning interval was 1°. 162 reflections were classified as unobserved [ $I < 1.96\sigma_1(I)$ , where  $\sigma_1(I)$  was derived from counting statistics]. Data were corrected for Lorentz and polarization effects and for absorption ( $\mu r = 0.83$ ). Transmission factors varied between 0.30 and 0.32. The density was determined pycnometrically in xylene at 298 K.

Table 1. Atomic coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and isotropic thermal parameters

$B_{\text{eq}}$  corresponds to non-H atoms,  $B$  to H atoms.  
 $B_{\text{eq}} = 4[V^2 \det(\beta_{ij})]^{1/3}$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B$ (Å <sup>2</sup> )
Co	4467.4 (4)	8400.5 (2)	5464.3 (3)	0.77 (1)
Na	5608 (2)	6573 (1)	4325 (1)	1.65 (3)
P(1)	2291.2 (9)	5309.4 (5)	5082.4 (5)	0.99 (1)
P(2)	7372.8 (8)	7236.4 (5)	6197.3 (5)	0.89 (1)
P(3)	4610.0 (8)	5298.1 (5)	2374.2 (5)	1.01 (1)
O(11)	3677 (3)	5733 (2)	5556 (2)	1.89 (3)
O(12)	942 (3)	5850 (1)	5323 (1)	1.42 (3)
O(13)	2238 (2)	4313 (1)	5292 (2)	1.30 (4)
O(21)	7385 (3)	7934 (2)	7005 (2)	1.51 (5)
O(22)	5999 (2)	7380 (1)	5648 (1)	1.21 (4)
O(23)	8821 (2)	7304 (1)	5710 (1)	1.26 (4)
O(31)	5035 (3)	4326 (2)	2034 (2)	2.11 (5)
O(32)	5154 (3)	5386 (2)	3325 (2)	1.64 (4)
O(33)	5146 (3)	6019 (1)	1731 (2)	1.52 (4)
O(4)	7858 (3)	7397 (2)	3816 (1)	1.41 (4)
H(1)	249 (5)	544 (3)	424 (3)	0.84
H(2)	723 (5)	640 (3)	659 (3)	0.75
H(3)	331 (5)	527 (3)	234 (3)	0.85
H(11)	415	537	600	2.25
H(21)	646	822	690	1.58
H(31)	475	420	140	2.17
H(41)	806	736	313	1.39
H(42)	801	799	399	1.39

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The position of the Co atom was obtained from a Patterson synthesis. The remaining non-H atoms were located by a Fourier synthesis. The H-atom positions were obtained from a difference electron density map after refinement of the positions and anisotropic temperature factors of all non-H atoms. H atoms were assigned the isotropic temperature factors of the atoms to which they are bonded. As the refined O—H bond distances became unrealistically short, another refinement was carried out in which all the H atoms except for H(1), H(2) and H(3) were fixed in the positions obtained from the difference map. After refinement of the positions and anisotropic temperature factors of the non-H atoms and of the positions of H(1) to H(3), the final  $R$  value = 0.046\* ( $R_w = 0.072$ ) was obtained for 1980 observed reflections. The weighting scheme used was  $w = 1/\sigma^2(F_o)$ , derived from  $\sigma(F_o)/|F_o| = \frac{1}{2}[\sigma_2(I)/I]$  and  $\sigma_2(I) = [\sigma_1^2(I) + (0.06I)^2]^{1/2}$ , where 0.06 corresponds to instrument instability. Unobserved reflections were not used in the refinement. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The maximum peak in the final difference map was 0.5 e  $\text{\AA}^{-3}$ , located 1.11  $\text{\AA}$  from the Co atom; the next nearest was 0.4 e  $\text{\AA}^{-3}$ , located 1.26  $\text{\AA}$  from the Na atom. The final positional and thermal parameters are given in Table 1. Calculations were carried out on an ICL 4-72 computer using the *TLS* program system (Sklenář & Petříček, 1981).

**Discussion.** The structure is depicted in Fig. 1 and the interatomic distances and angles are given in Table 2. In addition to the three crystallographically non-equivalent  $\text{HPO}_3$  tetrahedra, the structure also con-

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36834 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

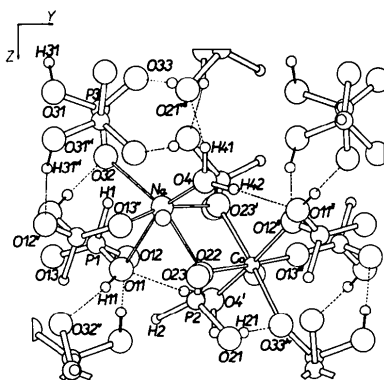


Fig. 1. The structural motif viewed along the  $x$  direction. Dotted lines between atoms represent hydrogen bonding. H(3) is hidden behind P(3).

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

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

P(1)—O(11)	1.566 (3)	Na—O(11)	2.809 (3)
O(12)	1.500 (3)	O(13 <sup>v</sup> )	2.413 (3)
O(13)	1.498 (2)	O(22)	2.312 (2)
H(1)	1.27 (4)	O(23 <sup>i</sup> )	2.313 (2)
P(2)—O(21)	1.573 (3)	O(32)	2.323 (3)
O(22)	1.500 (2)	O(4)	2.487 (3)
O(23)	1.499 (2)	Co—O(12 <sup>ii</sup> )	2.085 (2)
H(2)	1.37 (4)	O(13 <sup>iii</sup> )	2.062 (2)
P(3)—O(31)	1.563 (3)	O(22)	2.061 (2)
O(32)	1.493 (3)	O(23 <sup>i</sup> )	2.102 (2)
O(33)	1.504 (2)	O(33 <sup>iv</sup> )	2.145 (3)
H(3)	1.18 (5)	O(4 <sup>i</sup> )	2.151 (3)
O(11)—P(1)—O(12)	109.6 (1)	O(22)—P(2)—O(23)	117.2 (1)
O(11)—P(1)—O(13)	108.8 (1)	O(22)—P(2)—H(2)	106 (2)
O(11)—P(1)—H(1)	105 (2)	O(23)—P(2)—H(2)	111 (2)
O(12)—P(1)—O(13)	116.3 (1)		
O(12)—P(1)—H(1)	105 (2)	O(31)—P(3)—O(32)	107.5 (2)
O(13)—P(1)—H(1)	111 (2)	O(31)—P(3)—O(33)	111.3 (1)
		O(31)—P(3)—H(3)	102 (2)
		O(32)—P(3)—O(33)	115.2 (2)
O(21)—P(2)—O(22)	108.9 (1)	O(32)—P(3)—H(3)	112 (2)
O(21)—P(2)—O(23)	108.3 (1)	O(33)—P(3)—H(3)	109 (2)
O(21)—P(2)—H(2)	105 (2)		

Table 3. O...O distances ( $\text{\AA}$ ) in the indicated hydrogen bonds

O(11)...O(32 <sup>v</sup> )	2.560 (4)	O(4)...O(21 <sup>iii</sup> )	2.750 (3)
O(21)...O(33 <sup>iv</sup> )	2.578 (4)	O(4)...O(11 <sup>vii</sup> )	2.995 (4)
O(31 <sup>iii</sup> )...O(12 <sup>v</sup> )	2.688 (3)		

tains a water molecule and Co and Na atoms. The hydrogen bonds (Table 3) give rise to a three-dimensional network in which the O atoms can act as proton acceptors [O(12), O(32), O(33)] or as proton donors [O(31), O(4)], or even simultaneously as donors and acceptors [O(11), O(21)]. The Co and Na atoms are hexa-coordinated. Both are surrounded by octahedra made up of two O atoms from two different P(1) tetrahedra, two O atoms from two different P(2) tetrahedra, one O atom from the P(3) tetrahedron and one O atom from the water molecule. The Co and Na octahedra are bridged through the P(1) and P(2) atoms.

In the known phosphite structures,  $\text{LiH}_2\text{PO}_3$  (Philip-pot & Lindqvist, 1970, X-ray data; Johansson & Lindqvist, 1976, neutron data),  $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$  (Brodalla, Goeters, Kniep, Mootz & Wunderlich, 1978),  $\text{Na}_{0.5}\text{H}_{2.5}\text{PO}_3$  (Hazell, Hazell & Kratochvil, 1982),  $2\text{KH}_2\text{PO}_3 \cdot \text{H}_3\text{PO}_3$  (Loub & Paulus, 1981b),  $\text{MgHPO}_3 \cdot 6\text{H}_2\text{O}$  (Corbridge, 1956),  $\text{SnHPO}_3$  (McDon-ald & Eriks, 1980),  $\text{Sb}_2(\text{HPO}_3)_3$  (Loub & Paulus, 1981a),  $\text{MnH}_3\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  (Cisařová, Novák, Petříček, Kratochvil & Loub, 1982),  $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$  (Handlovič, 1969),  $\text{Cu}(\text{H}_2\text{PO}_3)_2$  (Handlovič, 1972),  $\text{Cd}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$  (Loub, Podlahová & Ječný, 1978),

P—OH distances from 1.529 to 1.579 Å and P—O from 1.471 to 1.550 Å were found. These values are in good agreement with the P—OH (mean value 1.564 Å) and P—O (mean value 1.499 Å) distances in Cd(H<sub>2</sub>PO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (Loub, Podlahová & Ječný, 1978), and H(42) atoms participate in hydrogen bonding of the anion–anion and water–anion types. The Na—O distances in the Na octahedron are comparable with those found in Na<sub>2</sub>HPO<sub>3</sub>·5H<sub>2</sub>O and Na<sub>0.5</sub>H<sub>2.5</sub>PO<sub>3</sub>, except for Na—O(11), which is much longer and is, in fact, among the longest found in the literature. The O—Na—O angles vary from 70.84 (9) to 113.50 (10)° and from 156.91 (8) to 163.03 (9)°. The Co octahedron is nearly regular (according to Table 2) without extreme values of the Co—O distances. The O—Co—O angles are in the range 84.75 (10)–95.27 (8)° and 173.77 (7)–175.68 (7)°.

The authors wish to thank Dr Eysseltoová for preparing the single crystals.

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*Acta Cryst.* (1982). **B38**, 2438–2441

## The Calcium Potassium Tetraborate Hydrate CaK<sub>2</sub>[B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O

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(Received 15 July 1981; accepted 16 March 1982)

**Abstract.** CaK<sub>2</sub>[B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *Z* = 4, *a* = 16.597 (2), *b* = 12.469 (2), *c* = 11.569 (2) Å, *V* = 2394.2 (1) Å<sup>3</sup>, *μ*(Mo *Kα*) = 0.698 mm<sup>-1</sup>, *D<sub>c</sub>* = 1.76 Mg m<sup>-3</sup>. The structure was solved with *MULTAN* and refined by means of full-matrix least-squares methods. The final *R* value is 0.052 for 3096 observed reflections. The Ca<sup>2+</sup> ion displays seven coordination, while the two non-equivalent K<sup>+</sup> ions display eight and six coordination. The crystal structure consists of alternate layers of anions and cations parallel to (100). Each tetraborate anion is hydrogen-bonded to two water molecules and the other tetraborate anion within a layer, while the alternate layers consist of three cations and six water molecules.

**Introduction.** A systematic structural study of borate compounds is being carried out by the Departments of

Crystallography and Mineralogy of the Universities of Oviedo and Barcelona. The title compound is the first tetraborate with two cations to have its crystal structure reported.

Colourless prismatic crystals were prepared by evaporation from aqueous solution. A crystal 0.50 × 0.06 × 0.1 mm was selected for measurement on a Philips PW1100 four-circle diffractometer. The unit cell was measured by centring 25 independent reflections and refining the orientation matrix and unit-cell parameters by least squares. A total of 3175 independent reflections within the range 2θ ≤ 60° were measured using graphite-monochromatized Mo *Kα* radiation, with 79 reflections rejected because of the imposed criterion *I* < 2.5σ(*I*), where σ(*I*) is the standard deviation based on counting statistics. Only Lorentz–polarization corrections were made.