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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{P}-\text{O}) = 0.002 \text{ \AA}$ 

Disorder in solvent or counterion

R factor = 0.018

wR factor = 0.057

Data-to-parameter ratio = 9.9

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Sodium cobalt(II) hydrogendiphosphate,  
 $\text{NaCoHP}_2\text{O}_7$ 

The title compound was prepared hydrothermally at 453 K. The structure consists of a three-dimensional framework built up from centrosymmetric  $\text{Co}_2(\text{HP}_2\text{O}_7)_2$  clusters, linked through P–O–Co corners, delimiting interconnected tunnels. The  $\text{Na}^+$  cations partially occupy two independent positions in the tunnels at a distance of  $0.58(2) \text{ \AA}$  from each other. The structure of  $\text{NaCoHP}_2\text{O}_7$  in the solid state is similar to that of  $\text{NaZnHP}_2\text{O}_7$  and  $\text{CaCoP}_2\text{O}_7$ .

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## Comment

The synthesis and structural characterization of metal phosphates are of great interest in terms of basic science, as well as applied research. In cobalt systems, several studies have been carried out on the incorporation of divalent cobalt cations into aluminium phosphates, due to their potential catalytic applications (Lin & Weng, 1993; Bu *et al.*, 1998). Several novel microporous cobalt phosphates with the formula  $M\text{CoPO}_4$  ( $M$  is an alkali metal or  $\text{NH}_4^+$ ) are related to the *ABW* zeolite framework topology (Feng *et al.*, 1997; Chippindale *et al.*, 1999; Henry *et al.*, 2000).

During our study of these systems, we have reported the synthesis and crystal structures of  $\text{Na}_2\text{Co}(\text{H}_2\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$  (Guesmi *et al.*, 2000) and  $\text{AgCo}_3\text{H}_2(\text{PO}_4)_3$  (Guesmi & Driss, 2002). These materials were prepared, respectively, at room temperature and by a hydrothermal method. In order to find new alkali–cobalt phosphate compounds, we have completed the investigation of  $A\text{—Co—P—O}$  systems ( $A$  is a monovalent cation) and have studied several parameters of the hydrothermal synthesis, such as the heating conditions. This paper describes the X-ray structure determination of a new cobalt(II) diphosphate synthesized hydrothermally.

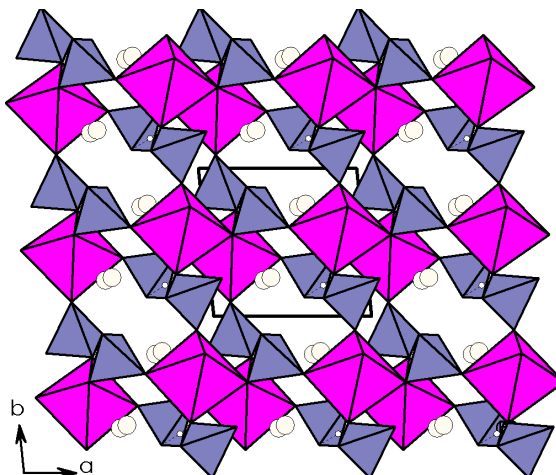
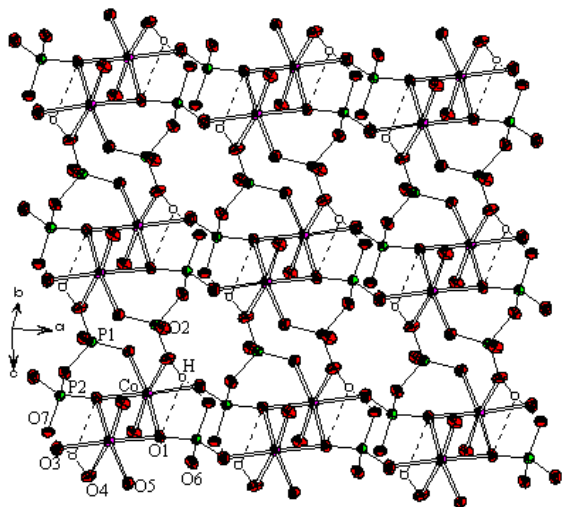


Figure 1

Projection of the  $\text{NaCoHP}_2\text{O}_7$  structure down the crystallographic  $c$  axis. Both partially occupied Na sites are shown.



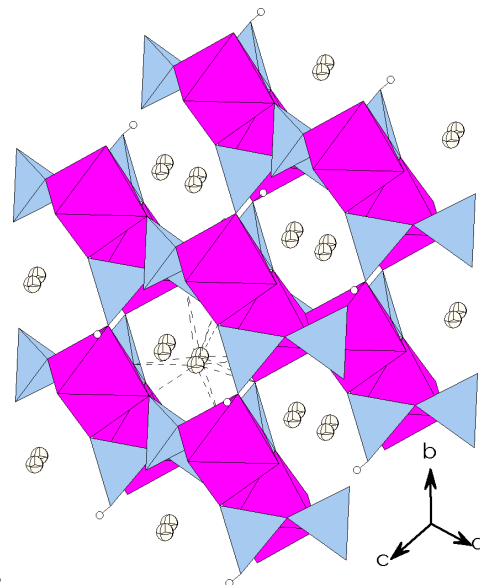
**Figure 2**  
The nature of the  $\text{Co}_2(\text{HP}_2\text{O}_7)_2$  cluster junction in the  $ac$  plane, with displacement ellipsoids drawn at the 80% probability level. Hydrogen bonds are shown by broken lines.

The structure of  $\text{NaCoHP}_2\text{O}_7$  consists of a three-dimensional framework of  $[\text{CoHP}_2\text{O}_7]^-$  anions. These anions are built up from edge-sharing  $\text{CoO}_6$  octahedra to form  $[\text{Co}_2\text{O}_{10}]$  units, which are linked to each other by diphosphate groups. Each  $\text{CoO}_6$  octahedron shares its six corners with five diphosphate groups. The  $\text{HP}_2\text{O}_7$  anion shares five of its six corners with three  $[\text{Co}_2\text{O}_{10}]$  units; the sixth corner participates in the coordination of the  $\text{Na}^+$  cations.

The interconnection between the metallic units and  $\text{HP}_2\text{O}_7$  groups results in centrosymmetric  $\text{Co}_2(\text{HP}_2\text{O}_7)_2$  clusters, which are linked through P—O—Co corners equally in all three directions. The hydrogen bonds act as an additional link within the structure (Brown, 1976). The resulting three-dimensional network delimits interconnected tunnels, which house the monovalent cations (Fig. 2).

The structure is related to that of  $\text{NaZnHP}_2\text{O}_7$  (Simonov *et al.*, 1991) and  $\text{CaCoP}_2\text{O}_7$  (Riou *et al.*, 1988). It differs from the zinc phosphate structure, in which there is no disorder of the  $\text{Na}^+$  cations and where the hydroxyl groups belong to bicoordinate O atoms. It differs also from  $\text{CaCoP}_2\text{O}_7$  by the replacement of  $\text{Ca}^{2+}$  by  $\text{Na}^+$  and a proton to balance the charge. However, the cell parameters of these two structures are very similar, because the radii of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  are similar.

On the basis of bond-length/bond-strength calculations (Brese & O'Keeffe, 1991), the Co and the P atoms are di- and pentavalent, respectively. A Co—O—P oxygen was found to be considerably undersaturated. To balance the charge, one H atom must be included in the formula. The valence sum, 1.58 calculated for O4, together with the longer P1—O4 bond length (1.555 Å), indicated that O4 should be a hydroxyl oxygen and O7 might be involved in hydrogen bonding [O4...O7 2.450 (3) Å]. The H atom was then located from a difference Fourier map, calculated at the final stage of the structure analysis. The  $\text{P}_2\text{O}_7$  anion has a nearly eclipsed conformation, with a torsion angle O5—P1—P2—O1 of 13.99 (8)°. The P—O6 bridge distance is, as expected, longer



**Figure 3**  
A [111] projection of the  $\text{NaCoHP}_2\text{O}_7$  structure, showing one type of tunnel containing  $\text{Na}^+$  cations. The Na—O interactions around both Na sites are shown as broken lines.

than the terminal ones; the mean values in the tetrahedra agree with the literature.

The Co—O distances range from 2.049 (2) to 2.210 (2) Å, the two longer distances corresponding to the tricoordinated O1 and O4 atoms of the common edge in the  $[\text{Co}_2\text{O}_{10}]$  units and the OH hydroxyl groups, respectively. The mean Co—O distance [2.13 (2) Å], smaller than that in  $\text{CaCoP}_2\text{O}_7$  (Riou *et al.*, 1988), is close to the sum of the ionic radii given by Shannon (1976) ( $\text{Co}^{2+}$  0.73 Å and  $\text{O}^{2-}$  1.40 Å). This indicates the ionic character of the cobalt environment.

When all atoms were anisotropically refined, a Fourier peak ( $1.02 \text{ e } \text{Å}^{-3}$ ) still remained close to the Na site. It was refined as an alternative sodium position, the refinement of the occupancy factors of both of the neighbouring  $\text{Na}^+$  cations leading to a small improvement of the reliability factors. Consequently, the  $\text{Na}^+$  cation is split into two independent positions with different occupancies. They are at a distance of 0.58 (2) Å from each other, and both are seven-coordinated, involving six common O atoms.

## Experimental

Single crystals of the title compound were prepared hydrothermally from an aqueous solution of  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  (Fluka, >97%),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Fluka, 99%) and  $\text{H}_3\text{PO}_4$  (Prolabo, 85%, density  $1.70 \text{ Mg m}^{-3}$ ) with an Na:Co:P atomic ratio of 4:1:4. A glass tube was quarter-filled with the mixture. After 72 h at 363 K, the tube was sealed and heated to 453 K for 20 d under autogenous pressure. Normal cooling to room temperature led to parallelepiped-shaped pink crystals of  $\text{NaCoHP}_2\text{O}_7$ , with an amorphous powder as the major product. The presence of Na, Co, and P was confirmed by EDS (energy dispersive spectroscopy) on a scanning electron microscope. IR spectroscopy proved the existence of the diphosphate group. The formula of the title compound,  $\text{NaCoHP}_2\text{O}_7$ , has been established as a result of its crystal structure investigation.

Crystal data

NaCoHP<sub>2</sub>O<sub>7</sub>  
*M<sub>r</sub>* = 256.87  
 Triclinic, *P* $\bar{1}$   
*a* = 6.5629 (7) Å  
*b* = 6.643 (1) Å  
*c* = 6.5309 (6) Å  
 $\alpha$  = 112.60 (1)°  
 $\beta$  = 87.935 (8)°  
 $\gamma$  = 96.14 (1)°  
*V* = 261.35 (5) Å<sup>3</sup>

Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.411, *T<sub>max</sub>* = 0.574  
 1246 measured reflections  
 1142 independent reflections  
 1123 reflections with *I* > 2 $\sigma$ (*I*)

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.018  
*wR*(*F*<sup>2</sup>) = 0.057  
*S* = 0.96  
 1142 reflections  
 115 parameters  
 H atoms restrained

*Z* = 2  
*D<sub>x</sub>* = 3.264 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 25  
 reflections  
 $\theta$  = 10.1–14.0°  
 $\mu$  = 3.96 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Parallelepiped, pink  
 0.25 × 0.18 × 0.14 mm

*R<sub>int</sub>* = 0.011  
 $\theta_{\text{max}}$  = 27.0°  
 $h$  = 0 → 8  
 $k$  = -8 → 8  
 $l$  = -8 → 8  
 2 standard reflections  
 frequency: 120 min  
 intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.5277P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.065 (4)

**Table 1**  
 Selected geometric parameters (Å).

Co1—O5 <sup>i</sup>	2.0495 (15)	Na—O5	2.341 (4)
Co1—O2	2.0782 (16)	Na—O7 <sup>iv</sup>	2.389 (4)
Co1—O3	2.1156 (16)	Na—O3	2.503 (7)
Co1—O1 <sup>ii</sup>	2.1474 (15)	Na—O7 <sup>ii</sup>	2.519 (6)
Co1—O1 <sup>iii</sup>	2.1713 (15)	Na—O1	2.622 (10)
Co1—O4	2.2104 (16)	Na—O2 <sup>ii</sup>	2.66 (2)
P1—O2 <sup>iv</sup>	1.5036 (16)	Na—O4	2.929 (13)
P1—O5 <sup>iii</sup>	1.5112 (16)	Na′—O5	2.295 (6)
P1—O4	1.5593 (16)	Na′—O7 <sup>iv</sup>	2.393 (7)
P1—O6 <sup>i</sup>	1.6121 (16)	Na′—O3	2.418 (6)
P2—O3	1.5103 (16)	Na′—O4	2.649 (14)
P2—O1	1.5394 (15)	Na′—O3 <sup>i</sup>	2.73 (3)
P2—O7	1.5414 (16)	Na′—O7 <sup>ii</sup>	2.75 (2)
P2—O6	1.5978 (15)	Na′—O1	2.95 (2)
Na—Na′	0.580 (17)		

Symmetry codes: (i) 1 - *x*, 1 - *y*, -*z*; (ii) 1 - *x*, 1 - *y*, 1 - *z*; (iii) *x* - 1, *y*, *z*; (iv) *x*, 1 + *y*, *z*.

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
O4—H···O7 <sup>ii</sup>	0.80	1.66	2.450 (2)	168
O4—H···O1 <sup>ii</sup>	0.80	2.56	2.955 (2)	111

Symmetry code: (ii) 1 - *x*, 1 - *y*, 1 - *z*.

The O4—H bond length was restrained to 0.80 (1) Å.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

References

Brandenburg, K. (1998). *DIAMOND*. Version 2.0. Crystal Impact GbR, Bonn, Germany.  
 Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.  
 Brown, I. D. (1976). *Acta Cryst.* **A32**, 24–31.  
 Bu, X., Gier, T. E., Feng, P. & Stucky, G. D. (1998). *Chem. Mater.* **10**, 2546–2551.  
 Chippindale, A. M., Cowley, A. R., Chen, J., Gao, Q. & Xu, R. (1999). *Acta Cryst.* **C55**, 845–847.  
 Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.  
 Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.  
 Feng, P., Bu, X., Tolbert, S. H. & Stucky, G. D. (1997). *J. Am. Chem. Soc.* **119**, 2497–2504.  
 Guesmi, A. & Driss, A. (2002). *Acta Cryst.* **C58**, i16–i17.  
 Guesmi, A., Zid, M. F. & Driss, A. (2000). *Acta Cryst.* **C56**, 511–512.  
 Henry, P. F., Hughes, E. M. & Weller, M. T. (2000). *J. Chem. Soc. Dalton Trans.* pp. 555–558.  
 Lin, S. S. & Weng, H. S. (1993). *Appl. Catal. A*, **105**, 289–308.  
 Macíček, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
 Riou, D., Labbe, P. & Goreaud, M. (1988). *C. R. Acad. Sci. Paris*, **307**, 1751–1756.  
 Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.  
 Simonov, M. A., Karpov, O. G., Dimitrova, O. V. & Strelkova, E. E. (1991). *Kristallografiya*, **36**, 1151–1154.