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$KHCoP_2O_7\cdot 2H_2O$: a novel acidic pyrophosphate

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Potassium cobalt hydrogenpyrophosphate dihydrate, $KHCoP_2O_7\cdot 2H_2O$, crystallizes in the orthorhombic space group *Pnma*. This salt is isotypic with $KHMP_2O_7\cdot 2H_2O$ (M = Mn and Zn). The structure consists of alternating layers, built from $HP_2O_7^{3-}$ acidic pyrophosphate groups and CoO_6 octahedra, joined by potassium ions and bridging hydrogen bonds. The Co, K and water O atoms lie on mirror planes. The pyrophosphate group consists of two symmetry-related PO_4 groups, with the bridging O atom on a mirror plane.

Comment

Hydrated or anhydrous pyrophosphates containing acidic anionic $[H_3P_2O_7]^-$, $[H_2P_2O_7]^{2-}$ or $[HP_2O_7]^{3-}$ entities are topics of widespread interest in the crystallographic literature (Corbridge, 1957; Dumas *et al.*, 1973; Mathew & Schroeder, 1977; Durif & Averbuch-Pouchot, 1982; Haromy-Tuli *et al.*, 1984; Effenberger, 1987; Haromy-Tuli *et al.*, 1990; Simonov *et al.*, 1991; Byrappa & Umesh Dutt, 1994; Hsu & Wang, 1999; Chehimi *et al.*, 2001; Blum *et al.*, 2002; Chehimi *et al.*, 2002; Ivashkevich *et al.*, 2002). The present paper is an extension of our earlier work on the acidic pyrophosphates that we have recently prepared and analyzed, *viz*. $KHMP_2O_7\cdot 2H_2O$ (M = Mn and Zn; Assaaoudi *et al.*, 2002) and $Na_4Mg_2(H_2P_2O_7)_4\cdot 8H_2O$ (Harcharras *et al.*, 2003). We report here the crystal structure of a new pyrophosphate compound, *viz*. $KHCoP_2O_7\cdot 2H_2O$.

The pyrophosphate group consists of two symmetry-related PO_4 groups, with the bridging atom (O1) in a special position. The Co-atom octahedron and pyrophosphate groups are depicted in Figs. 1(*a*) and 1(*b*). The three-dimensional structure is built from acidic pyrophosphate–Co^{II} layers stacked along the *c* axis (Fig. 2), alternating with layers of K^+ ions. The Co^{2+} ions are octahedrally surrounded by four O atoms from three different pyrophosphate anions and by two water molecules (Table 1).

It is possible to distinguish three types of P—O distances, *viz*. P—O1 bonds [1.618 (2) Å; the longest bonds] corresponding to the bridging O atoms, P—O2 bonds [1.541 (2) Å] involving hydroxyl groups, and P—O3/4 bonds corresponding

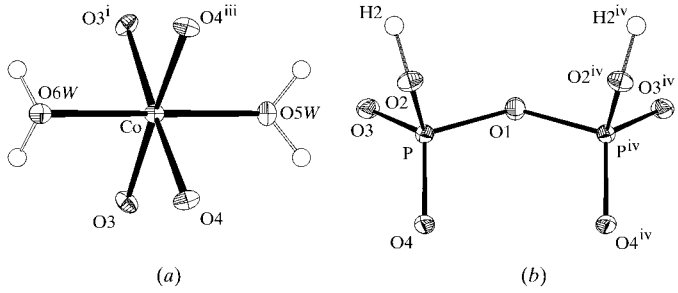

Figure 1
Views of (*a*) the $CoO_4(H_2O)^{2+}$ coordination polyhedron and (*b*) the pyrophosphate group. Displacement ellipsoids are shown at the 50% probability level. Symmetry codes are as in Table 1.

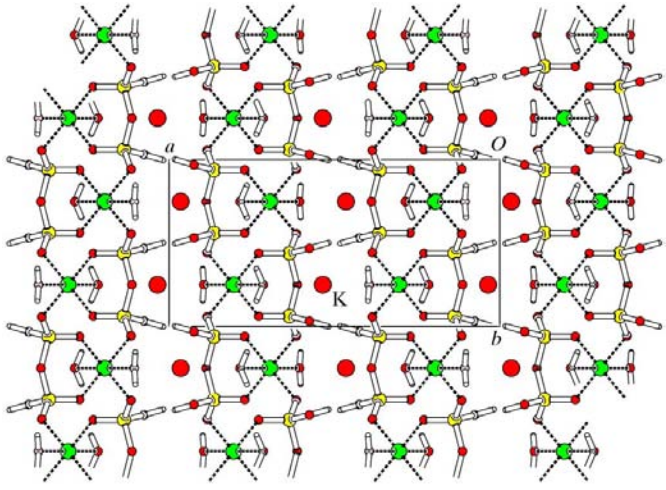

Figure 2
Projections of the crystal structure along the *c* axis, showing the network of pyrophosphate and $CoO_4(H_2O)$ groups.

to the external O atoms [mean 1.502 (2) Å; the shortest bonds]. The $HP_2O_7^{3-}$ anions show an eclipsed conformation, with a P—O—P bridging angle of 130.5 (2)°; the average O—P—O angle is 109.4°. Details of the bridging hydrogen bonds are given in Table 2.

Experimental

An aqueous solution of cobalt dichloride hexahydrate, $CoCl_2\cdot 6H_2O$ (0.1 *M*), was added dropwise to a solution of $K_4P_2O_7$ (0.1 *M*). Anhydrous tetrapotassium pyrophosphate, $K_4P_2O_7$, was prepared by dehydration of K_2HPO_4 at 873 K for 6 h. The pH of the mixture of these two solutions was controlled with concentrated hydrochloric acid. The solution was left at room temperature and crystals, identified as $KHCoP_2O_7\cdot 2H_2O$, appeared in the solution after 4 d.

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Crystal data

$KHCoP_2O_7{\cdot}2H_2O$
M_r = 309.01
Orthorhombic, *Pnma*
a = 15.4724 (15) Å
b = 7.7881 (8) Å
c = 6.4942 (6) Å
V = 782.56 (14) Å^3
Z = 4
D_x = 2.623 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 955 reflections
θ = 2.6–27.5°
μ = 3.16 mm^{-1}
T = 250 K
Plate, colourless
0.20 × 0.20 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: empirical (*MULABS*; Blessing, 1995)
T_{min} = 0.569, T_{max} = 0.669
4664 measured reflections
955 independent reflections
955 observed reflections
R_{int} = 0.041
θ_{max} = 27.5°
$h = -15 \rightarrow 20$
$k = -10 \rightarrow 8$
$l = -7 \rightarrow 8$

Refinement

Refinement on F^2
$R(F)$ = 0.034
$wR(F^2)$ = 0.039
S = 1.37
955 reflections
80 parameters
H-atom parameters constrained
$w = 1/\{900 + 0.01[\sigma(F_o^2)^2] + 0.01/(\sigma F_o^2)\}$
$(\Delta/\sigma)_{max}$ = 0.042
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.97 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 1.63 (12) × 10^3

Table 1
Selected geometric parameters (Å, °).

Co—O3^{i}	2.110 (2)	P^{iv}—O1^{iv}	1.618 (2)
Co—O4	2.065 (2)	P^{iv}—O2^{iv}	1.541 (2)
Co—O5*W*	2.146 (4)	P^{iv}—O3^{iv}	1.499 (2)
Co—O6*W*	2.159 (4)	P^{iv}—O4^{iv}	1.505 (2)
O1^{iv}—P^{iv}—O2^{iv}	106.01 (15)	O2^{iv}—P^{iv}—O4^{iv}	110.59 (13)
O1^{iv}—P^{iv}—O3^{iv}	104.03 (16)	O3^{iv}—P^{iv}—O4^{iv}	115.72 (12)
O1^{iv}—P^{iv}—O4^{iv}	108.56 (14)	P^{v}—O1^{iv}—P^{iv}	130.5 (2)
O2^{iv}—P^{iv}—O3^{iv}	111.23 (12)		

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

Table 2
Hydrogen bonding geometry (Å,°).

D—H···A	D—H	H···A	D—A	D—H···A
O5*W*–H5*W*···O2	0.96 (3)	1.86 (3)	2.817 (3)	178 (4)
O6*W*–H6*W*···O4	0.96 (3)	1.85 (3)	2.679 (3)	143 (3)

H atoms were located from difference Fourier maps and were restrained to lie 0.96 Å from their carrier atoms, with fixed displacement parameters of 0.035 Å^2. Atom H2 was split into two half-occupied positions around a center of inversion.

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *DIRDIF*96 (Beurskens *et al.*, 1996); program(s) used to refine structure: *CRYLSQ* in *Xtal*3.7 (Hall *et al.*, 2000); molecular graphics: *PLATON* (Spek, 2003), *ORTEP* (Johnson, 1970) and *PLUTON* (Spek, 1991); software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.7, and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1135). Services for accessing these data are described at the back of the journal.

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