Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Dipotassium cobalt(II) bis(hydrogenphosphite) dihydrate, $K_2Co(HPO_3)_2\cdot 2H_2O$

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Received 1 March 2004
Accepted 31 March 2004
Online 24 April 2004

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(P–O) = 0.002 Å
R factor = 0.022
wR factor = 0.069
Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

$K_2Co(HPO_3)_2\cdot 2H_2O$ is a new phosphite within the K–T–H_3PO_3 system (T = divalent transition metal cation). Its structure can be described as a three-dimensional network made up of KO_6 and HPO_3 polyhedra, which share corners and edges. In the cavities of this framework, Co^{2+} ions are located in an almost regular octahedral oxygen coordination. An IR study has confirmed the presence of HPO_3 hydrogenphosphite groups.

Comment

Neutral phosphites are obtained by neutralization of phosphorous acid solutions by appropriate bases until pH 8 is reached. Acid phosphites are obtained by dissolution of corresponding bases in solutions of H_3PO_3 up to pH 3.4. When cations of alkali metals, ammonium, divalent or trivalent 3d metals or magnesium are used, phosphorous acid forms a series of salts with chemical formulae containing various types of groups such as HPO_3^{2-} or $H_2PO_3^-$: LiH_2PO_3 (Philippot & Lindqvist, 1970), $Na_2HPO_3\cdot 5H_2O$ (Colton & Henn, 1971; Brodalla *et al.*, 1978), KH_2PO_3 (Kratochvíl *et al.*, 1983), $K_2(H_2PO_3)_2(H_3PO_3)$ (Loub & Paulus, 1981), $NH_4H_2PO_3$ (Melichar *et al.*, 1984), $Zn(H_2PO_3)_2\cdot x(H_2O)$ [$x = 3$ (Ortiz-Avila *et al.*, 1989), $x = 0.33$ (Durand *et al.*, 1992)], $M(H_2PO_3)2\cdot xH_2O$ [Mg (x = 6, Corbridge, 1956), Cr (x = 2, Brynda *et al.*, 1987)], $M_{11}(HPO_3)_8(OH)_6$ [M = Mn, Fe (Attfield & Morris, 1994) and Ni (Marcos, Amoros, Beltran-Polte *et al.*, 1993)], $M(HPO_3)\cdot H_2O$ [Co (Sapina *et al.*, 1989), Ni (Marcos, Amoros, Sapine *et al.*, 1993)], $CuHPO_3\cdot 2H_2O$ (Handlovič, 1965; Handlovič, 1969; El Bali & Massa, 2002). On the other hand, only a few crystal structures of mixed alkali/3d metal phosphites have been

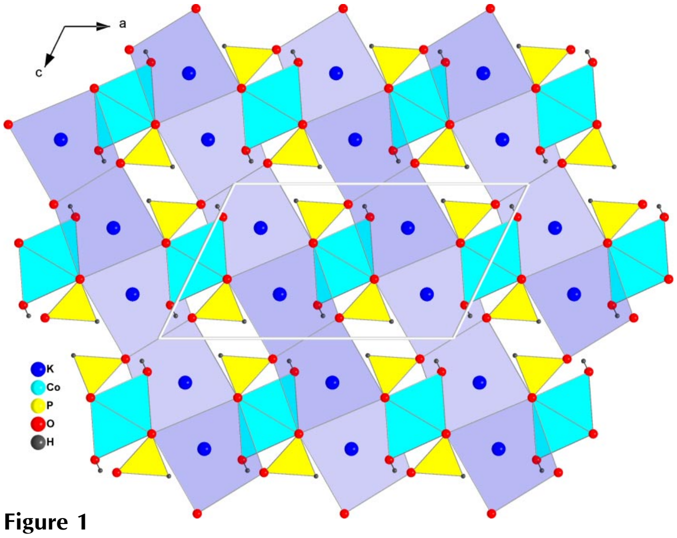

Figure 1
Projection of the crystal structure along the monoclinic axis. Polyhedra colour key: cyan (CoO_6), yellow (HPO_3), transparent blue (KO_6).

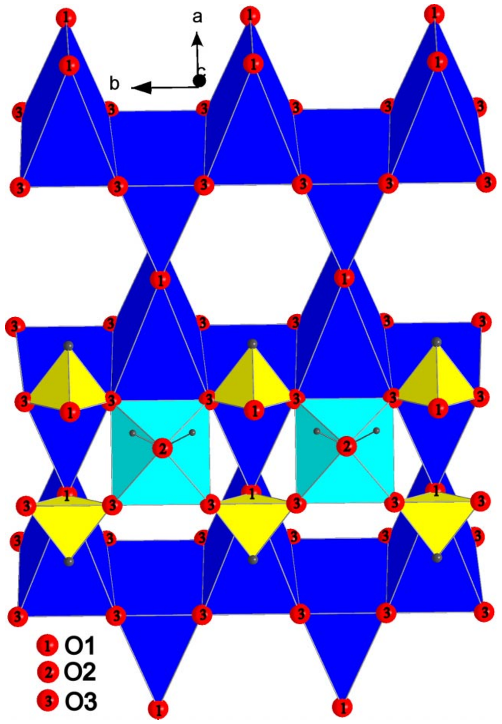

Figure 2
Details of a KO_6 sheet and of an adjacent HPO_3/CoO_6 chain.

reported so far. The structures already known are: Na*T*($H_2PO_3)_3\cdot H_2O$, with *T* = Mn (Chmelíková *et al.*, 1986) and *T* = Co (Kratochvíl *et al.*, 1982), $A_2Zn_3(HPO_3)_4$ with *A* = Na, K (Ortiz-Avila *et al.*, 1989) and $(NH_4)_2Zn_5(HPO_3)_6\cdot 4H_2O$ (Gordon & Harrison, 2002).

To obtain reliable crystallographic data within the *A*–*T*–H_3PO_3 system, where *T* is a divalent 3*d* metal and *A* is Na or K, we carried out systematic investigations. The expected results should allow a deeper insight into the structural peculiarities of this phosphite family. During these studies, we have recently reported the structural results obtained from single crystals of Na*M*$(H_2PO_3)\cdot 2H_2O$, *M* = Zn (Ouarsal *et al.*, 2002), Mg (Ouarsal *et al.*, 2003), and we are currently investigating the Ni member of this series. The present paper deals with the synthesis, crystal structure and IR investigation of the new mixed phosphite material, $K_2Co(HPO_3)_2\cdot 2H_2O$.

As shown in Fig. 1, the HPO_3 tetrahedra and CoO_6 octahedra share corners, forming a chain in the direction of the monoclinic *b* axis. The connection between the chains is mediated by sheets of KO_6 polyhedra perpendicular to the *ac* plane. A detailed view of a KO_6 sheet and an adjacent HPO_3/CoO_6 chain is given in Fig. 2. The KO_6 polyhedra share the edges O3—O3 and O1—O1 while the connection between HPO_3 and CoO_6 is realised *via* the apical atom O3. The CoO_6 octahedron shares the edge O3—O3 with the KO_6 sheet and the opposite edge O3′—O3′ with the neighbouring parallel sheet that is not present in the figure. The tetrahedron HPO_3 shares the edge O3—O3 and the corner O1 as well as the opposite corner/edge with the parallel (not plotted) sheet. In Fig. 3 details of the oxygen coordination around K, Co and P are shown.

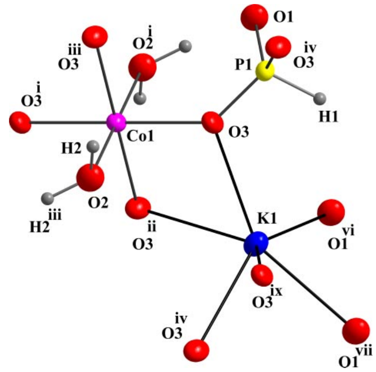

Figure 3
Details of bonding in the structure of $K_2Co(HPO_3)_2\cdot 2H_2O$. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, y, 1 - z$; (iii) $x, -y, z$; (iv) $x, 1 - y, z$; (v) $x, 1 + y, z$; (vi) $x, y, 1 + z$; (vii) $1 - x, 1 - y, 1 - z$; (viii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ix) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (x) $1 - x, 1 + y, 1 - z$; (xi) $x, y, z - 1$; (xii) $x, y - 1, z$; (xiii) $1 - x, -y, -z$; (xiv) $1 - x, y, -z$.

The hydrogenphosphite group is approximately tetrahedral [angles 110.18 (12)–114.39 (10)°]. The H1 atom bonded to phosphorus is not involved in any hydrogen bonding. The average P—O distance and O—P—O angle are 1.512 Å and 110.5 °, respectively. These values lie in the same range as the ones previously reported for $CuHPO_3\cdot 2H_2O$ (El Bali & Massa, 2002) or for $CaZn(HPO_3)_2\cdot 2H_2O$ (Shieh *et al.*, 1990) [1.525 Å and 111.86 °].

The coordination sphere around Co^{2+} is made up from four monodentate HPO_3^{2-} entities arranged in an almost square configuration [*d*(Co—O3) = 2.017 Å, with angles O3—Co—O3 ranging from 89.89 to 90.10°]. The two remaining vertices of the octahedron are occupied by two O2 atoms belonging to water molecules with *d*(Co—O2) = 2.174 Å. In the distorted octahedron, the average Co—O distance of 2.105 Å is close to the values reported for $Co(HPO_3)\cdot H_2O$ (2.107 Å) or for $NaCo(H_2PO_3)_3\cdot H_2O$ (2.167 Å). In the structure of the title compound, the CoO_6 octahedra are isolated. The Co···Co distance is 5.319 Å, which is longer than the corresponding value in $NaCo(H_2PO_3)_3\cdot H_2O$ (4.993 Å).

The K^+ cation is coordinated by four monodentate and one bidentate hydrogenphosphite entities. The geometry of the polyhedron might be described as that of a distorted trigonal prism. The distance *d*(K—O) ranges from 2.726 (4) to 2.869 (4) Å, with an average of 2.789 Å, which is near the values reported for KH_2PO_3 (2.936 Å) and $KH_2PO_3\cdot H_3PO_3$ (2.78 Å).

The IR spectrum of $K_2Co(HPO_3)_2\cdot 2H_2O$ (Fig. 4) shows the presence of vibrational bands at 564, 996 and 1160 cm^{-1}, characteristic for a PO_3 group. The intense bands near 2360 cm^{-1} are associated with the stretching vibration of the P—H bond. The vibrational modes at 1630 and 3440 cm^{-1} are assigned to the symmetric and asymmetric vibrations of the water molecule.

Experimental

The compound was prepared by reacting 2 mmol of KCl (Merck, > 99%) and 0.8 mmol of $CoCO_3$ (Merck, > 99%) in 10 ml 0.1 *M* phosphorous acid (H_3PO_3). The mixture was stirred for 1 h at 333 K.

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The solution containing a pink precipitate was left at room temperature. After three weeks, small well shaped pink crystallites were filtered out and washed with 80% ethanol.

Crystal data

$K_2Co(HPO_3)_2(H_2O)_2$
$M_r = 333.1$
Monoclinic, $C2/m$
$a = 12.538$ (6) Å
$b = 5.319$ (2) Å
$c = 7.327$ (4) Å
$\beta = 116.02$ (5)°
$V = 439.1$ (4) Å^3
$Z = 2$

$D_x = 2.518$ Mg m^{-3}
Mo Kα radiation
Cell parameters from 40 reflections
$\theta = 10$–15°
$\mu = 3.28$ mm^{-1}
$T = 295$ K
Prism, light pink
0.30 × 0.10 × 0.10 mm

Data collection

Oxford Diffraction diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (*JANA*2000; Petricek & Dusek, 2000)
$T_{min} = 0.651$, $T_{max} = 0.708$
1048 measured reflections
583 independent reflections
474 reflections with $I > 3\sigma(I)$

$R_{int} = 0.019$
$\theta_{max} = 28.0°$
$h = 0 \rightarrow 16$
$k = -7 \rightarrow 7$
$l = -9 \rightarrow 8$
3 standard reflections every 100 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 3\sigma(F^2)] = 0.022$
$wR(F^2) = 0.070$
$S = 1.22$
583 reflections
45 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/(\sigma^2(I) + 0.0016I^2)$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Co1—O2	2.175 (4)	P1—O3^{iv}	1.5158 (19)
Co1—O2^{i}	2.175 (4)	P1—H1	1.34 (3)
Co1—O3	2.0702 (16)	K1—O1^{v}	2.771 (3)
Co1—O3^{i}	2.0702 (16)	K1—O1^{vi}	2.734 (3)
Co1—O3^{ii}	2.0702 (16)	K1—O3	2.889 (2)
Co1—O3^{iii}	2.0702 (16)	K1—O3^{vii}	2.7257 (18)
Co1—H2	2.50 (7)	K1—O3^{viii}	2.7257 (18)
Co1—H2^{i}	2.50 (7)	K1—O3^{iv}	2.889 (2)
Co1—H2^{ii}	2.50 (7)	K1—H2^{i}	2.82 (5)
Co1—H2^{iii}	2.50 (7)	K1—H2^{ix}	2.82 (5)
P1—O1	1.512 (4)	O2—H2	0.85 (4)
P1—O3	1.5158 (19)	O2—H2^{iii}	0.85 (4)

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

Both H atoms were located in a difference Fourier map. H1 was refined with the P1—H1 distance restrained to 1.3 Å. The U_{iso}(H) value of H2 was constrained to be $1.2U_{eq}$(O2).

Data collection: *KM4B8* (Galdecki *et al.*, 1996); cell refinement: *KM4B8*; data reduction: *JANA*2000 (Petricek & Dusek, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997); program(s) used to refine structure: *JANA*2000; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *JANA*2000.

B. El Bali thanks Professor B. El Ouadi (Université La Rochelle, France) for his kind collaboration.

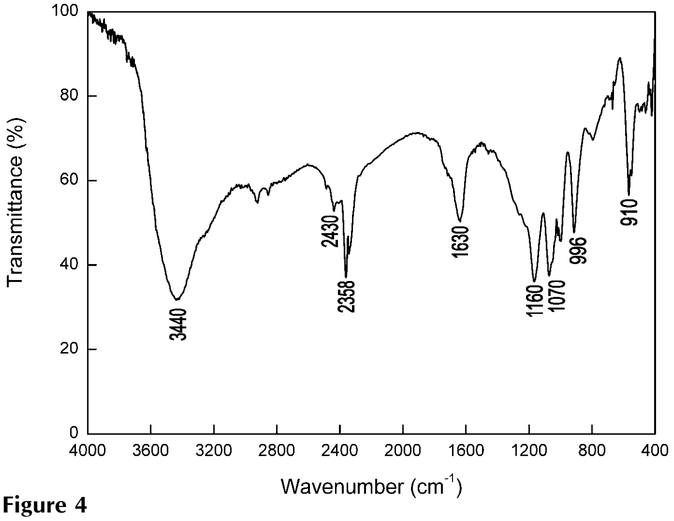

Figure 4
IR spectrum of $K_2Co(HPO_3)_2{\cdot}2H_2O$.

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