

$(\text{NH}_4)_2[\text{Co}(\text{H}_2\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_2]$

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Key indicators

Single-crystal X-ray study

$T = 301 \text{ K}$

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

R factor = 0.034

wR factor = 0.085

Data-to-parameter ratio = 11.7

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

Diammonium cobalt(II) dihydrogendiphosphate(V) dihydrate is a member of the isotypic series $(\text{NH}_4)_2T(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ ($T = \text{Mn}, \text{Ni}$ or Zn). Isolated almost-regular CoO_6 octahedra form a layered structure. The IR spectrum shows bands characteristic of $\text{H}_2\text{P}_2\text{O}_7$ groups.

Comment

The preparation and crystal structures of diphosphates have been studied for a long time in some detail (Durif, 1995, and reference therein). However, there are only a few structural reports on acidic diphosphates with the formula $A_2T(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot x\text{H}_2\text{O}$, where A = alkaline or ammonium and T = divalent $3d$ metal. The acidic diphosphates form an important class of phosphates with many applications (Essehli *et al.*, 2005a). We previously reported a series of compounds with the formula $\text{K}_2T(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$, with $T = \text{Mn}$ (Tahiri *et al.*, 2003), Co (Alaoui Tahiri *et al.*, 2002), Ni (Tahiri *et al.*, 2004) and Zn (Alaoui Tahiri *et al.*, 2003). Recently, we published also a new phosphate $(\text{NH}_4)_2\text{Zn}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (Essehli *et al.*, 2005a; Capitelli *et al.*, 2005), which is isotypic with its Mn analogue (Capitelli *et al.*, 2004). We report here the crystal structure of the Co member of this series. The crystal structure of the Ni member of this series will be published elsewhere (Essehli *et al.*, 2005b).

Co^{2+} cations occupy crystallographic inversion centres in the framework of the crystal structure. The metal atoms constitute a primitive, nearly hexagonal lattice. They are

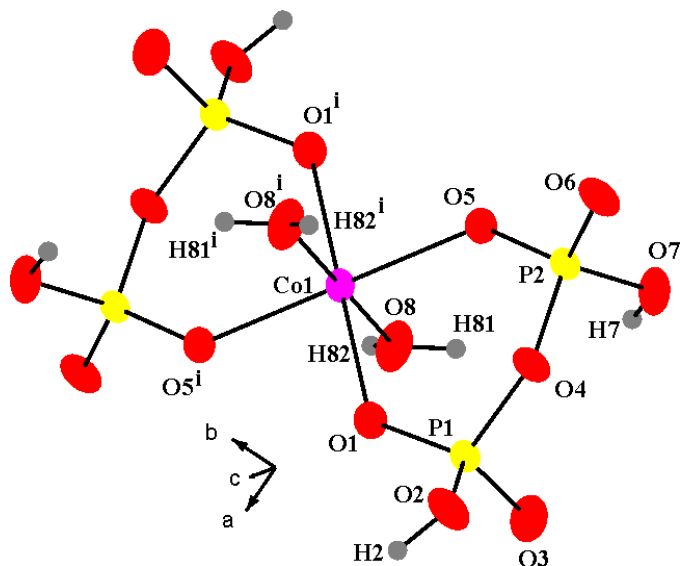


Figure 1

The coordination scheme around P^{V} and Co^{II} atoms in $(\text{NH}_4)_2\text{Co}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$. The probability level of the anisotropic displacement ellipsoids is 50%. [Symmetry code: (i) $-x, 1-y, -z$.]

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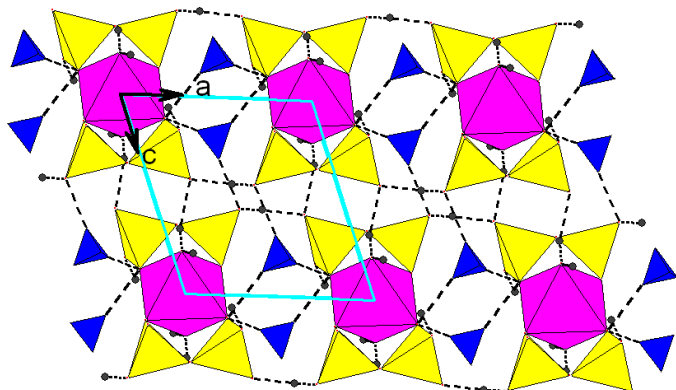


Figure 2

Projection of the crystal structure along [010]. Yellow polyhedra: $\text{H}_2\text{P}_2\text{O}_7$, pink: CoO_6 , blue: NH_4^+ ; dark grey spheres: H atoms. Dashed lines represent hydrogen bonds.

octahedrally surrounded by four O atoms from two bidentate $\text{H}_2\text{P}_2\text{O}_7$ groups and by two O atoms from the water molecules. This coordination scheme has almost regular D_{4h} idealized symmetry. The CoO_6 polyhedra are isolated in the framework of $(\text{NH}_4)_2\text{Co}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ with $\text{Co} \cdots \text{Co}$ distances over 7 Å. The average $\text{Co}-\text{O}$ distance of 2.106 Å is in close agreement with the isotopic Zn compound (2.084 Å) and is comparable with the average of 2.114 Å found in $\text{Co}_2\text{P}_2\text{O}_7$ (El Bali & Bolte, 2002).

Each of the two unique P atoms is coordinated in a slightly distorted tetrahedral geometry by four O atoms, two of which belong to hydroxyl groups. The two tetrahedra share an apex (O4) to form the $\text{H}_2\text{P}_2\text{O}_7^{2-}$ diphosphate anion in a roughly eclipsed conformation. The average $\text{P}-\text{O}$ distance of 1.545 Å is comparable to the values of other diphosphates: 1.533 Å in $(\text{NH}_4)_2\text{Zn}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$, 1.537 Å in $\text{K}_2\text{H}_2\text{P}_2\text{O}_7$ (Larbot *et al.*, 1983) and 1.543 Å in $\text{K}_3\text{H}(\text{H}_2\text{P}_2\text{O}_7)_2$ (Dumas, 1978). The $\text{P}-\text{O}-\text{P}$ bridging angle of the bent dihydrogendiphosphate anion in $(\text{NH}_4)_2\text{Co}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ is 131.3 (1)°. This is close to the values observed in $(\text{NH}_4)_2\text{Zn}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ [128.85 (6)°], $(\text{NH}_4)_2\text{Mn}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (131.7°), $\text{K}_2\text{Zn}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (130.8°) and $\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ (130.3°; Robertson & Calvo, 1967). Fig. 1 illustrates the oxygen coordination scheme around P^{V} and Co^{II} in the title compound.

The crystal structure of $(\text{NH}_4)_2\text{Co}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ might be thus described as a complex made of isolated $[\text{Co}(\text{H}_2\text{O})_2(\text{H}_2\text{P}_2\text{O}_7)]^{2-}$ and NH_4^+ ions interacting with each other through intricate hydrogen bonding, as shown in Fig. 2. There are three kinds of hydrogen bonds (see Table 2), *viz.* four bonds from ammonium, two from the dihydrogendiphosphate units and another two from water molecules. Note that the longest hydrogen bonds occur between the hydroxyl species of the $\text{H}_2\text{P}_2\text{O}_7$ groups.

The interpretation and assignment of IR bands of $(\text{NH}_4)_2\text{Co}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (see Table 3) can be made in terms of PO_2 groups, POH groups, the $\text{P}-\text{O}-\text{P}$ bridge, as well as NH_4^+ and H_2O (Sarr & Diop, 1987). These data confirm the presence of the different entities in the title compound. In general, the region between 900 and 1200 cm^{-1} shows vibration bands that are characteristic for diphosphates.

Experimental

Crystals of the title compound were obtained by mixing three aqueous solutions, namely NH_4OH (20 ml, 0.1 M), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{K}_4\text{P}_2\text{O}_7$ (30 ml, 0.1 M). The mixture was stirred for a day and allowed to stand for around three weeks. At the end of this time, large prismatic light pink crystals were deposited, which were filtered off and washed with a water–ethanol solution (20:80). The IR spectrum of the title compound was recorded from a KBr pellet on a Perkin–Elmer 1750 spectrometer in the spectral range between 4000 and 400 cm^{-1} .

Crystal data

$(\text{NH}_4)_2[\text{Co}(\text{H}_2\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_2]$
 $M_r = 482.96$
 Triclinic, $P\bar{1}$
 $a = 7.067$ (1) Å
 $b = 7.368$ (1) Å
 $c = 7.852$ (1) Å
 $\alpha = 81.23$ (1)°
 $\beta = 70.68$ (1)°
 $\gamma = 88.54$ (1)°
 $V = 381.18$ (9) Å³

$Z = 1$
 $D_x = 2.104$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2045 reflections
 $\theta = 2.8$ – 26.0 °
 $\mu = 1.63$ mm⁻¹
 $T = 301$ (2) K
 Prism, pink
 $0.20 \times 0.16 \times 0.06$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector
 ω scans
 Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2001)
 $T_{\text{min}} = 0.736$, $T_{\text{max}} = 0.909$

2547 measured reflections
 1520 independent reflections
 1359 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$
 $\theta_{\text{max}} = 26.4$ °
 $h = -8 \rightarrow 8$
 $k = -7 \rightarrow 9$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.085$
 $S = 1.02$
 1520 reflections
 130 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.4707P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.033$
 $\Delta\rho_{\text{max}} = 0.80$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.50$ e Å⁻³

Table 1

Selected bond lengths (Å).

Co1—O8	2.094 (2)	P1—O3	1.511 (2)
Co1—O8 ⁱ	2.094 (2)	P1—O2	1.557 (2)
Co1—O1 ⁱ	2.0942 (19)	P1—O4	1.6126 (19)
Co1—O1	2.0942 (19)	P2—O6	1.5050 (19)
Co1—O5	2.1289 (18)	P2—O5	1.5063 (19)
Co1—O5 ⁱ	2.1289 (18)	P2—O7	1.561 (2)
P1—O1	1.4995 (19)	P2—O4	1.610 (2)

Symmetry code: (i) $-x, 1 - y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H2...O6 ⁱ	0.899 (10)	1.606 (11)	2.505 (3)	179 (4)
O7—H7...O3 ⁱⁱ	0.891 (10)	1.648 (12)	2.533 (3)	171 (4)
O8—H81...O3 ⁱⁱⁱ	0.844 (10)	1.941 (10)	2.781 (3)	174 (3)
O8—H82...O6 ^{iv}	0.840 (10)	1.931 (11)	2.766 (3)	173 (4)
N1—H11...O5 ^v	0.899 (9)	2.164 (11)	3.048 (3)	168 (2)
N1—H12...O2 ^{iv}	0.897 (9)	1.993 (10)	2.878 (3)	168 (2)
N1—H13...O5	0.897 (9)	2.088 (13)	2.974 (3)	169 (3)
N1—H14...O7 ^{iv}	0.899 (9)	2.089 (10)	2.984 (3)	174 (3)

Symmetry codes: (ii) $1 + x, y, z$; (iii) $-x, -y, -z$; (iv) $x, 1 + y, z$; (v) $-x, 1 - y, -1 - z$; (vi) $-1 - x, 1 - y, -z$.

Table 3
IR spectroscopic data (cm⁻¹).

IR bands	Mode assignment
3242	OH stretching
3119	NH stretching
2871–2738	NH ₄ ⁺ combination modes
1658	OH ₂ bending
1313	OH ₂ bending
1446–1332	NH ₄ ⁺ bending
1176–1079	P–O stretching
936	asymmetric P–O–P stretching
731	symmetric P–O–P stretching
538–488	P–O bending modes and NH ₄ ⁺ torsional oscillation

All H atoms were located in a difference Fourier map. Water H atoms were refined with constrained geometry (Nardelli, 1999), *viz.* O–H distances were constrained to 0.85 Å and H–O–H angles to 107°; the H···H distance was constrained to 1.365 Å, thus leading to the angle of 107°. H atoms of NH₄ were refined with constrained geometry for tetrahedra, with an N–H distance of 0.9 Å. H atoms of the OH groups were refined with the O–H distance constrained to 0.9 Å. The displacement parameters of all H atoms were constrained to 1.2U_{eq} of the parent atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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