

Reinvestigation of  $\text{NH}_4[\text{Co}(\text{H}_2\text{O})_6]\text{PO}_4$  based on single-crystal dataBrahim El Bali,<sup>a\*</sup> Rachid Essehli,<sup>a</sup>  
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## Key indicators

Single-crystal X-ray study  
 $T = 293 \text{ K}$   
Mean  $\sigma(\text{P–O}) = 0.003 \text{ \AA}$   
 $R \text{ factor} = 0.029$   
 $wR \text{ factor} = 0.066$   
Data-to-parameter ratio = 11.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The structure of the title compound, ammonium hexaqua-cobalt(II) orthophosphate, known from powder data, has been refined based on single-crystal data. The compound crystallizes in the struvite  $[\text{NH}_4\text{Mg}(\text{H}_2\text{O})_6\text{PO}_4]$  structure type and is isotypic with the homologous nickel phase. The framework is built of  $\text{NH}_4^+$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $\text{PO}_4^{3-}$  ions stacked in two kinds of ribbons parallel to (010).  $\text{Co}^{\text{II}}$  atoms are well separated in the framework, with the shortest  $\text{Co} \cdots \text{Co}$  distance being over  $6 \text{ \AA}$ .

## Comment

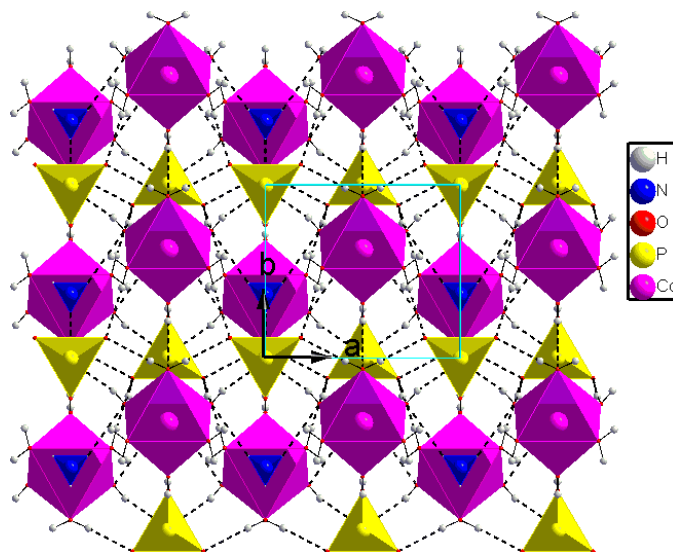
A survey of the literature on hydrated orthophosphate phases of the formula type  $\text{NH}_4T(\text{H}_2\text{O})_x\text{PO}_4$  ( $T$  is a divalent  $3d$  metal) shows that only a few crystal structures have been published previously, viz.  $\text{NH}_4\text{Co}(\text{H}_2\text{O})\text{PO}_4$  (Duc Tran *et al.*, 1968; Yakubovich *et al.*, 1999),  $\text{NH}_4\text{Co}(\text{H}_2\text{O})_6\text{PO}_4$  (Touaiher *et al.*, 2001),  $\text{NH}_4\text{Ni}(\text{H}_2\text{O})_6\text{PO}_4$  (Blachnik *et al.*, 1997) and  $\text{NH}_4\text{Cu}(\text{H}_2\text{O})\text{PO}_4$  (Pujana *et al.*, 1998). There are also numerous anhydrous phases, such as  $\text{NH}_4\text{ZnPO}_4$  (Bu *et al.*, 1997; Harrison *et al.*, 2001).

For ammonium cobalt(II) orthophosphate(V) hexahydrate,  $\text{NH}_4\text{Co}(\text{H}_2\text{O})_6\text{PO}_4$ , structural data based on powder X-ray diffraction refinements were reported (Touaiher *et al.*, 2001). Furthermore, the structure was published without H-atom positions and with an  $R$  value of 0.08. During our investigations of other types of phosphates in solution, we obtained crystals of the title compound serendipitously. In comparison

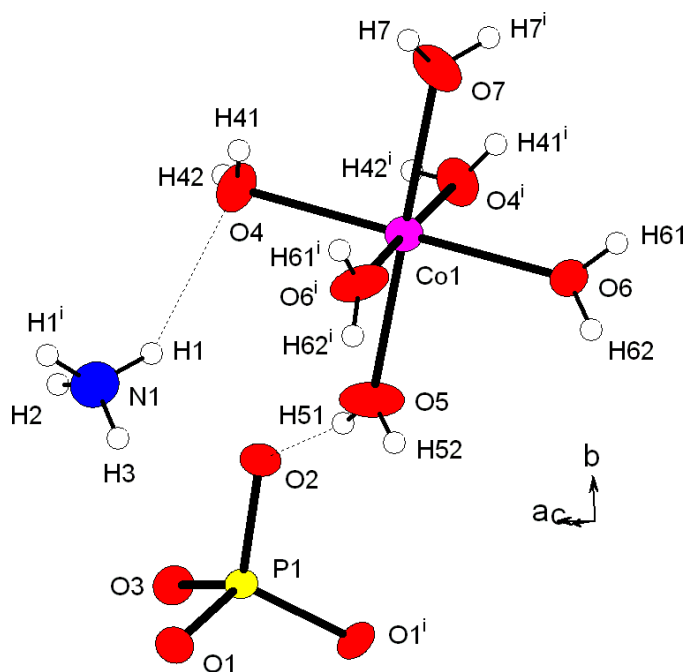
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**Figure 1**  
Projection of the crystal structure along  $[001]$ , shown in a polyhedral representation. Hydrogen bonds are indicated by dashed lines.



**Figure 2**

Coordination of  $\text{Co}^{\text{II}}$  and  $\text{P}^{\text{V}}$  atoms in the structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres with an arbitrary radius. [Symmetry code: (i)  $-x, y, z$ .]

with the powder refinement, we have now located the H-atom positions, together with a higher precision of the structural data.

The three-dimensional network of  $\text{NH}_4[\text{Co}(\text{H}_2\text{O})_6]\text{PO}_4$  consists of isolated  $[\text{NH}_4]$ ,  $[\text{Co}(\text{H}_2\text{O})_6]$  and  $[\text{PO}_4]$  polyhedra. The structure can be described in terms of ribbons parallel to (010), an association of cationic ribbons (R1) and anionic ribbons (R2). R1 might then be formulated as  $[\text{NH}_4 \cdot \text{Co}(\text{H}_2\text{O})_6]^{3+}$ , composed of  $\text{NH}_4^+$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , whereas R2 is built of  $\text{PO}_4^{3-}$  orthophosphate ions. The structure is characterized by an intricate hydrogen-bonding network (Table 2), with strong O(water)–H $\cdots$ O(phosphate) hydrogen bonds; the ammonium ions also donate their H atoms to build up strong hydrogen bonds with phosphate O atoms (see dashed lines in Fig. 1).

The P atom is tetrahedrally coordinated by four O atoms. The  $\text{PO}_4$  tetrahedra are isolated in the structure. The average P–O distance is 1.542 Å, a value which is close to the corresponding distance of 1.537 Å obtained from the powder refinement (Touaiher *et al.*, 2001) or 1.537 Å in  $\text{Co}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (Anderson *et al.*, 1976).

The  $\text{Co}^{2+}$  ion is surrounded in a slightly distorted octahedral coordination by water O atoms. The average Co–O distance of 2.077 Å is slightly longer than the value reported from the powder refinement (2.055 Å). The  $[(\text{Co}(\text{H}_2\text{O})_6)]$  octahedra are isolated in the structure, the shortest distance between two neighbouring  $\text{Co}^{2+}$  ions being 6.157 (1) Å, which is marginally longer than the distance obtained from the powder refinement (6.146 Å). Fig. 2 shows the coordination polyhedra around the Co and P atoms in the structure.

## Experimental

Dark purple crystals were found in a solution containing  $\text{RbNO}_3$  (1 mol),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (1 mol),  $\text{H}_3\text{PO}_4$  (0.5 mol) and  $(\text{NH}_4)_2\text{HPO}_4$  (0.5 mol). The mixture was used for the preparation of a mixed phosphate which was not obtained. The deposited large crystals were filtered off and washed with a solution of 80% ethanol.

### Crystal data

$(\text{NH}_4)[\text{Co}(\text{H}_2\text{O})_6](\text{PO}_4)$   
 $M_r = 280.04$   
 Orthorhombic,  $Pmn2_1$   
 $a = 6.946$  (2) Å  
 $b = 6.157$  (2) Å  
 $c = 11.172$  (6) Å  
 $V = 477.8$  (3) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.947$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 4521 reflections  
 $\theta = 5.5$ – $29.5^\circ$   
 $\mu = 2.00$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, purple  
 $0.80 \times 0.25 \times 0.25$  mm

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\text{min}} = 0.230$ ,  $T_{\text{max}} = 0.610$   
 3846 measured reflections  
 1136 independent reflections

1016 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.047$   
 $\theta_{\text{max}} = 27.6^\circ$   
 $h = -8 \rightarrow 9$   
 $k = -7 \rightarrow 8$   
 $l = -13 \rightarrow 14$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.066$   
 $S = 1.08$   
 1136 reflections  
 99 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.39$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 472 Friedel pairs  
 Flack parameter = 0.07 (2)

**Table 1**

Selected bond lengths (Å).

Co1–O6	2.057 (3)	Co1–O7	2.130 (4)
Co1–O6 <sup>i</sup>	2.057 (3)	P1–O3	1.538 (4)
Co1–O4	2.089 (2)	P1–O1	1.540 (2)
Co1–O4 <sup>i</sup>	2.089 (2)	P1–O1 <sup>i</sup>	1.540 (2)
Co1–O5	2.129 (4)	P1–O2	1.549 (3)

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
O5–H51 $\cdots$ O2	0.71 (2)	1.97 (3)	2.666 (6)	169 (8)
N1–H1 $\cdots$ O4	0.81 (3)	2.29 (4)	3.010 (5)	147 (6)
O4–H41 $\cdots$ O3 <sup>ii</sup>	0.70 (2)	2.09 (3)	2.688 (3)	143 (5)
O7–H7 $\cdots$ O1 <sup>ii</sup>	0.71 (2)	1.94 (2)	2.642 (3)	172 (6)
O6–H61 $\cdots$ O2 <sup>iii</sup>	0.71 (2)	1.95 (3)	2.622 (3)	158 (6)
O4–H42 $\cdots$ O1 <sup>iv</sup>	0.71 (2)	1.95 (3)	2.629 (4)	163 (5)
O5–H52 $\cdots$ O7 <sup>v</sup>	0.71 (2)	2.32 (2)	3.034 (6)	180 (7)
O6–H62 $\cdots$ O1 <sup>vi</sup>	0.69 (4)	1.97 (5)	2.661 (3)	176 (6)
N1–H2 $\cdots$ O6 <sup>vii</sup>	0.82 (3)	2.49 (3)	3.171 (6)	142 (3)
N1–H3 $\cdots$ O3 <sup>viii</sup>	0.81 (3)	1.97 (3)	2.782 (6)	176 (9)

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

H atoms were located in a difference Fourier map. Similarity restraints were applied to all O–H distances and to N–H distances. Common  $U_{\text{iso}}$  values were refined for the H atoms bonded to oxygen

and for those bonded to nitrogen. Constraints on the N–H and O–H bond distances coupled with average displacement parameters for the H atoms were applied in the final refinement cycles.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *COLLECT* (Nonius, 1998); data reduction: *EVALCCD* (Nonius, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999) and *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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## References

- Altomare, A., Burla, M. C., Camalli, M., Casciarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Anderson, J., Kostiner, E. & Ruzsala, F. A. (1976). *Inorg. Chem.* **15**, 2744–2748.
- Blachnik, R., Wiest, T., Duellmer, A. & Reuter, H. (1997). *Z. Kristallogr.* **212**, 20–23.
- Brandenburg, K. (1999). *DIAMOND*. Version. 2.1c. Crystal Impact GbR, Bonn, Germany.
- Bu, X.-H., Feng, P.-Y., Gier, T. E. & Stucky, G. D. (1997). *Zeolites*, **19**, 200–208.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Duc Tran, Q., Durif, A., Guitel, J. C. & Averbuch-Pouchot, M. T. (1968). *Bull. Soc. Chim. Fr.* pp. 1759–1760.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Harrison, W. T. A., Sobolev, A. N. & Phillips, M. L. F. (2001). *Acta Cryst.* **C57**, 508–509.
- Nonius (1997). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Pujana, A., Pizarro, J. L., Lezama, L., Goni, A., Arriortua, M. I. & Rojo, T. (1998). *J. Mater. Chem.* **8**, 1055–1060.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Touaiher, M., Bettach, M., Benkhouja, K., Zahir, M., Aranda, M. A. G. & Bruque, S. (2001). *Ann. Chim. (Paris)*, **26**, 49–54.
- Yakubovich, O. V., Karimova, O. V., Dimitrova, O. V. & Massa, W. (1999). *Acta Cryst.* **C55**, 151–153.