

Co_{0.50}VOPO₄·2H₂O**Lianxia Meng, Yuping Ma, Xiaoliang Zhang and Yan Xu***

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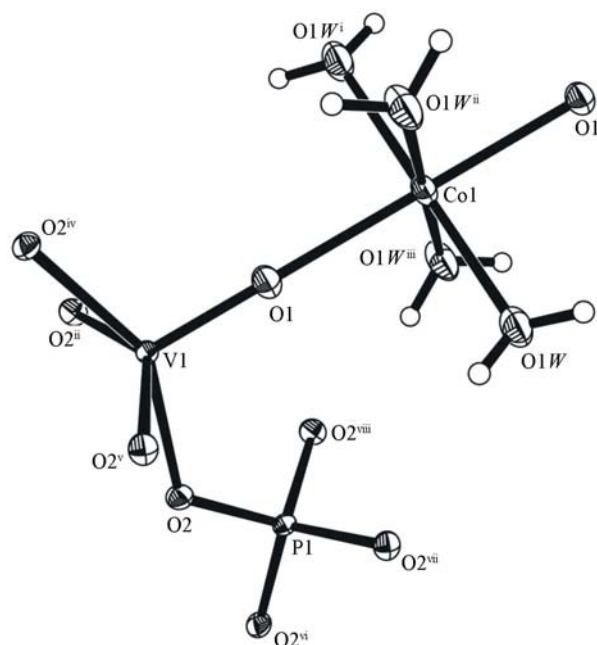
The crystal structure of cobalt vanadophosphate dihydrate {systematic name: poly[diaqua- μ -oxido- μ -phosphato-hemicobalt(II)vanadium(II)]}, Co_{0.50}VOPO₄·2H₂O, shows a three-dimensional framework assembled from VO₅ square pyramids, PO₄ tetrahedra and Co[O₂(H₂O)₄] octahedra. The Co^{II} ions have local 4/*m* symmetry, with the equatorial water molecules in the mirror plane, while the V and apical O atom of the vanadyl group are located on the fourfold rotation axis and the P atoms reside on $\bar{4}$ sites. The PO₄ tetrahedra connect the VO₅ polyhedra to form a planar P–V–O layer. The [Co(H₂O)₄]²⁺ cations link adjacent P–V–O layers *via* vanadyl O atoms to generate an unprecedented three-dimensional open framework. Powder diffraction measurements reveal that the framework collapses on removal of the water molecules.

Comment

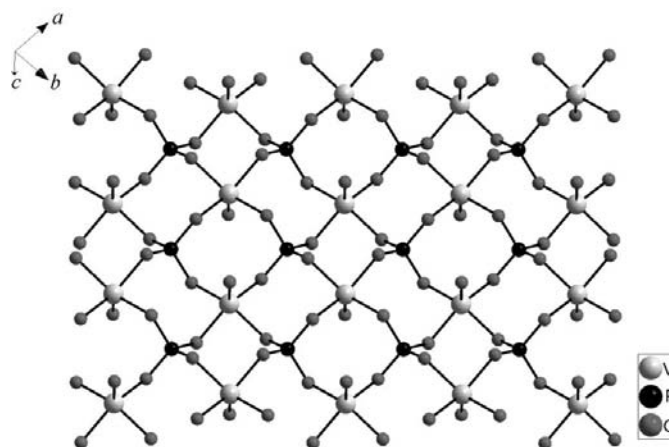
Over the past few decades, the synthesis of solid-state inorganic materials with new topological structures built up of oxygen polyhedra has received much attention because of the functional applications of these materials in ion-exchange, adsorption, catalysis and radioactive waste remediation. As the tetrahedral building elements of polyhedral frameworks, not only Si and Ge but also P have been chosen for the synthesis of inorganic materials (Li *et al.*, 1998; Xu *et al.*, 2004, 2006). In the past few years, an important advance in layered materials has been the study of vanadophosphates (Soghomonian *et al.*, 1993; Huang *et al.*, 2001; Cui *et al.*, 2004). Our research concentrates on connecting V–P–O layers *via* transition metals to make new three-dimensional inorganic materials. As part of this work, we designed and synthesized the title compound, which features a three-dimensional framework constructed from V–P–O layers and [Co(H₂O)₄]²⁺ cations.

The asymmetric unit of Co_{0.50}VOPO₄·2H₂O contains nine crystallographically independent non-H atoms (Fig. 1). The octahedrally coordinated Co1 atom is located on the origin with 4/*m* symmetry. The four coordinated water molecules

(O1W) are located in the equatorial (mirror) plane. Atom V1 is coordinated by five O atoms in a typical square pyramid. Both the V atom and the apical O atom are on the fourfold rotation axis. The basal O atoms, which are shared with the P atoms, make O–V–O angles of 85.632 (14) and 147.96 (5)°. The short apical V–O distance (Table 1) indicates a vanadyl-type interaction (V=O). The V atom carries a formal oxidation state of +4, which is confirmed by bond-valence sum calculations [$S = (R/R_0)^{-N} = 4.0024$; Brown & Altermatt, 1985]. Atom P1 of the tetrahedral phosphate group is located on a special position of $\bar{4}$ symmetry. Each V atom makes four V–O–P linkages, and the polyhedra thus connect to produce a very flat VOPO₄ layer (Fig. 2), which is similar to that found

**Figure 1**

The molecular structure of the title compound, with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-y, x, z$; (iii) $y, -x, -z$; (iv) $-x, -y, z$; (v) $y, -x, z$; (vi) $-x+1, -y, z$; (vii) $y+\frac{1}{2}, -x+\frac{1}{2}, -z-\frac{1}{2}$; (viii) $-y+\frac{1}{2}, x-\frac{1}{2}, -z-\frac{1}{2}$.]

**Figure 2**

The structure of a single V–P–O layer.

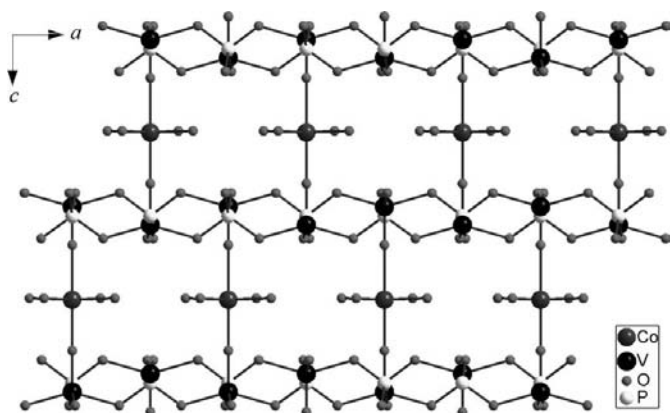


Figure 3
Stacking of the layers and linkage via $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$ groups. Note the open spaces between the tetraaquacobalt(II) groups.



Figure 4
The channels along the b axis, showing the secondary building unit consisting of two CoO_6 octahedra (dark gray), two PO_4 tetrahedra (light gray) and four VO_5 square pyramids (black).

in the previously reported compounds $(\text{NH}_4)\text{VOPO}_4 \cdot 1.5\text{H}_2\text{O}$ (Do *et al.*, 2000a), $\text{Na}_{0.5}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{K}_{0.5}\text{VOPO}_4 \cdot 1.5\text{H}_2\text{O}$ (Wang *et al.*, 1991), and $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{VO}(\text{VO}_2)\text{PO}_4]_2$ (Do *et al.*, 2000b). In contrast to these phases, the interlayer ammonium or alkali metal cations are replaced by $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$ cations that coordinate to the vanadyl O atoms and thus link adjacent layers to generate a three-dimensional framework (Fig. 3). To the best of our knowledge, this is the first example in which a transition metal (Co^{2+}) connects flat V–O–P layers. The layers, which are 7.44 (2) Å apart, contain channels running along the b -axis direction. These secondary building units are constructed from four VO_5 square pyramids, two PO_4 tetrahedra and two CoO_6 octahedra (Fig. 4). In the reported three-dimensional vanadophosphates with larger 10-polyhedron ring channels (Zhang *et al.*, 1995; Chen *et al.*, 2006), templating organic amines are located in the channels.

Thermal analysis of $\text{Co}_{0.50}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ under an N_2 atmosphere shows a one-step mass loss of 15.85% between 573 and 623 K, with no further loss up to 1073 K. The total weight loss is in excellent agreement with the calculated weight loss for desorption of coordinated water. Powder X-ray diffraction indicates that the inorganic framework collapses completely after the removal of water.

Experimental

The title crystal was synthesized by a hydrothermal reaction using NH_4VO_3 (0.2339 g), $\text{Co}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (Ac is acetyl; 0.2490 g) and water (10 ml) in a molar ratio of 2:1:555. The mixture was adjusted to pH 3 with H_3PO_4 (50%), placed in a 25 ml Teflon-lined autoclave and heated at 443 K for 7 d. After the sample had been cooled to room temperature, washed with distilled water, filtered and dried in air, block-shaped green crystals of the title compound were obtained. The reduction of vanadium from +5 to +4 may be due to reaction with acetic acid, which may act as a reducing agent at low pH.

Crystal data

$\text{Co}_{0.50}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$
 $M_r = 227.41$
Tetragonal, $I4/m$
 $a = 6.2570$ (5) Å
 $c = 13.400$ (2) Å
 $V = 524.62$ (10) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 3.69 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 $0.13 \times 0.12 \times 0.12 \text{ mm}$

Data collection

Bruker APEXII CCD
diffractometer
Absorption correction: multi-scan
(SADABS; Sheldrick, 2003)
 $T_{\min} = 0.645$, $T_{\max} = 0.666$

1403 measured reflections
275 independent reflections
274 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.040$
 $S = 1.20$
275 reflections
30 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.53 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

Co1—O1W	2.0442 (15)	V1—O2	1.9764 (9)
Co1—O1	2.1189 (19)	P1—O2	1.5383 (9)
V1—O1	1.5986 (19)	O1W—H1	0.815 (13)

The unique H atom of the water molecule was located in a difference map and included in the refinement with the H—O bond length restrained to 0.82 (2) Å and with the $U_{\text{iso}}(\text{H})$ value fixed at $1.5U_{\text{eq}}(\text{O1W})$.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3194). Services for accessing these data are described at the back of the journal.

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