

# Tetraaquacobalt(II) bis[vanadyl(IV) phosphate], $[\text{Co}(\text{H}_2\text{O})_4][\text{VO}(\text{PO}_4)]_2$

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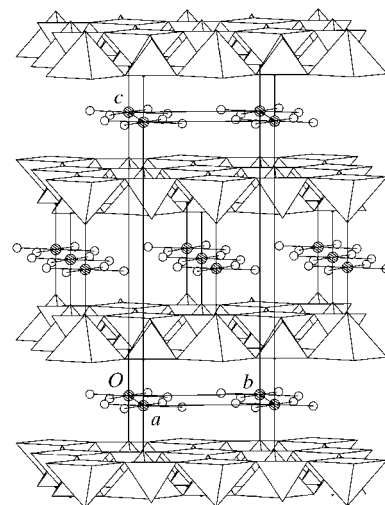
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The structure of  $[\text{Co}(\text{H}_2\text{O})_4][\text{VO}(\text{PO}_4)]_2$  is composed of  $[\text{VO}(\text{PO}_4)]$  layers and interlayer tetrahydrated  $\text{Co}^{2+}$  ions. Alternating  $\text{VO}_5$  square pyramids and  $\text{PO}_4$  tetrahedra share O-atom vertices, thus forming the vanadyl phosphate layers. Two vanadyl oxo groups from neighbouring layers are coordinated to each Co atom in a *trans* fashion, with Co—O distances of 2.157 (4) Å, thus generating a three-dimensional framework structure.

## Comment

Vanadium phosphate systems are of interest because of their catalytic properties and their diverse structural characteristics (Zubieta, 1994). To date, the V/P/O phases have been shown to possess a wide variety of structural types as a result of the different coordination geometries of vanadium (*e.g.* octahedra, square pyramids, trigonal bipyramids and tetrahedra; Pope & Müller, 1991) and the different linkages between vanadium polyhedra and phosphate tetrahedra. Some examples of these phases are  $\text{AVO}(\text{PO}_4)$  (Haushalter *et al.*, 1994),  $A[\text{VO}(\text{PO}_4)]_2$  (Grandin *et al.*, 1992) and  $A_{0.5}\text{VO}(\text{PO}_4)\cdot n\text{H}_2\text{O}$  (Kang *et al.*, 1991), where *A* is an alkali or alkaline earth metal cation. Further structural diversity can be achieved by introducing other inorganic and organic cations into this system (Duan *et al.*, 2003). In the present paper, we report the hydrothermal synthesis and crystal structure of a new member of the *A/V/P/O* class of solids (*A* is a transition metal cation), *viz.*  $[\text{Co}(\text{H}_2\text{O})_4][\text{VO}(\text{PO}_4)]_2$ , (I).

The crystal structure of (I) consists of vanadyl phosphate layers, with  $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$  units located in the interlayer positions (Fig. 1). The coordination spheres around the V and Co atoms in the asymmetric unit of (I) are shown in Fig. 2. The V atom exhibits a square-pyramidal geometry involving a vanadyl oxo group with a short V—O bond distance of 1.624 (4) Å and four basal O atoms with an equivalent V—O distance of 1.9959 (16) Å (Table 1). Valence-sum calculations (Brown & Altermatt, 1985) resulted in a value of 3.897 for the V site, which is very close to the ideal value of 4 for  $\text{V}^{\text{IV}}$ . The coordination octahedron around the Co atom has  $D_{4h}$

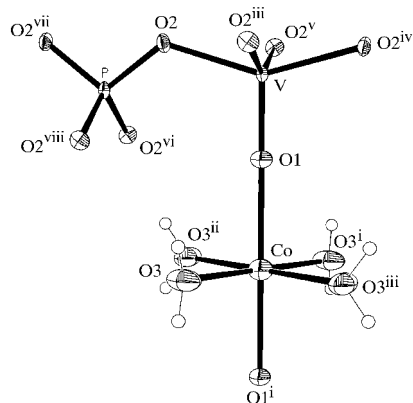


**Figure 1**

A representation of the structure of (I), viewed along the *a* axis, showing the vanadyl phosphate layers fused by  $\text{VO}_5$  square pyramids and  $\text{PO}_4$  tetrahedra. These layers are connected via covalent Co—O interactions into a three-dimensional framework. The striped and open circles denote, respectively, O atoms attached to Co atoms and water O atoms. H atoms have been omitted for clarity.

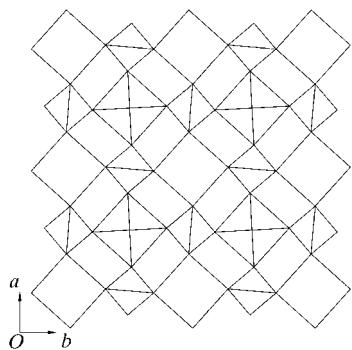
symmetry. The four equatorial O atoms, from four water molecules, have Co—O bond lengths of 2.064 (3) Å, and the two axial O atoms, from the vanadyl oxo atoms of two adjacent layers, each has a Co—O distance of 2.157 (4) Å.

A view perpendicular to one of the layers is illustrated in Fig. 3. The layer is a four-connected net of corner-sharing  $\text{VO}_5$  square pyramids and  $\text{PO}_4$  tetrahedra. Each  $\text{VO}_5$  pyramid shares its four basal O atoms with four different  $\text{PO}_4$  groups. Along the [110] direction, the vanadyl O atoms alternately point up and down relative to the layer. Two neighbouring layers are aligned so as to order the oxo groups of the vanadyl sites directly towards one another along the *c* axis, and the two corresponding vanadyl oxo atoms are coordinated to a Co



**Figure 2**

The asymmetric unit in the structure of (I), with displacement ellipsoids at the 50% probability level, showing the coordination environment around the P and metal atoms. [Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $y, -x, -z$ ; (iii)  $-y, x, z$ ; (iv)  $-x, -y, z$ ; (v)  $y, -x, z$ ; (vi)  $\frac{1}{2} - y, x - \frac{1}{2}, \frac{1}{2} - z$ ; (vii)  $1 - x, -y, z$ ; (viii)  $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$ .]


**Figure 3**

A view perpendicular to one of the vanadyl phosphate layers in (I), showing the connectivities between the  $\text{VO}_5$  square pyramids and the  $\text{PO}_4$  tetrahedra.

atom in a *trans* fashion, such that a linear  $\text{V}=\text{O}-\text{Co}-\text{O}=\text{V}$  group is formed (Fig. 1). Therefore, the structure of (I) can be described as vanadyl phosphate layers connected *via* covalent  $\text{Co}-\text{O}$  interactions into a three-dimensional open framework.

Compound (I) belongs to the family of compounds with the general composition  $A_{0.5}[\text{VO}(\text{PO}_4)] \cdot n\text{H}_2\text{O}$  ( $n = 2$  or  $1.5$ ), whose structures can be topologically derived from the parent layered compound  $\text{VO}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  (Tietz, 1981). The layers in  $\text{VO}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  are constructed *via* the alternation of vanadium octahedra and phosphate tetrahedra. The introduction of a mono- or divalent metal cation not only leads to the partial or full reduction of  $\text{V}^{5+}$  to  $\text{V}^{4+}$  but also affects the way that the layers are stacked relative to one another and the arrangement of water molecules between the layers, so as to accommodate the second metal ions. While the Na, K, Ca, Sr (Kang *et al.*, 1991) and Cu (Zhang *et al.*, 1995) compounds of the family are layered, the structures of  $A_{0.5}[\text{VO}(\text{PO}_4)] \cdot 1.5\text{H}_2\text{O}$  ( $A = \text{Ni}$  and  $\text{Pb}$ ; Tietz, 1981; Lii & Mao, 1992) exhibit three-dimensional architectures built from  $\text{V}^{\text{IV}}\text{O}_6$  octahedra,  $\text{PO}_4$  tetrahedra and  $\text{AO}_6$  octahedra. In contrast, the three-dimensional network of (I) comprises  $\text{V}^{\text{IV}}\text{O}_5$  square pyramids,  $\text{PO}_4$  tetrahedra and  $\text{CoO}_6$  octahedra connected *via* shared corners, and the stacking of the vanadyl phosphate layers in (I) can be viewed as the relative shifting of neighbouring parent layers in  $\text{VO}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  along the  $[110]$  direction by  $(a + b)/2$ . There is extensive hydrogen bonding in the structure of (I), as listed in Table 2. These hydrogen bonds make the crystal structure of (I) more stable.

## Experimental

Compound (I) was synthesized hydrothermally under autogenous pressure. A mixture of  $\text{NH}_4\text{VO}_3$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$  (85%),  $\text{Na}_2\text{MoO}_4 \cdot 6\text{H}_2\text{O}$ , hexamethylenetetramine and  $\text{H}_2\text{O}$  in the molar ratio 2:1:1.5:1:0.5:492 was sealed in a 17 ml Teflon-lined autoclave and heated at 433 K for 90 h. The reaction mixture was cooled slowly to room temperature at a rate of  $8 \text{ K h}^{-1}$  and green plate-like crystals of (I) were obtained. The crystals were filtered off, washed with distilled water and dried in air (45% yield based on vanadium). The pH of the system increased from 5.2 before heating to 6.3 at the end of the reaction. The IR spectrum of (I) exhibits a strong band at  $995 \text{ cm}^{-1}$

which was attributed to  $\nu(\text{V}-\text{O})$ , and features at 1118 and  $1027 \text{ cm}^{-1}$  which are related to  $\text{PO}_4$ . The weight loss of (I) in the range 538–663 K is 15.89%, in agreement with the calculated removal of the water molecules associated with the  $\text{Co}^{2+}$  cations (15.85%). Analysis calculated for  $\text{H}_8\text{CoO}_{14}\text{P}_2\text{V}_2$ : P 13.62, V 22.40, Co 12.96%; found: P 13.72, V 22.28, Co 12.91%.

### Crystal data

$[\text{Co}(\text{H}_2\text{O})_4][\text{VO}(\text{PO}_4)]_2$   
 $M_r = 454.81$   
 Tetragonal,  $I4/m$   
 $a = 6.307 (1) \text{ \AA}$   
 $c = 13.615 (3) \text{ \AA}$   
 $V = 541.58 (17) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 2.789 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 80 reflections  
 $\theta = 5-15^\circ$   
 $\mu = 3.58 \text{ mm}^{-1}$   
 $T = 296 (2) \text{ K}$   
 Plate, green  
 $0.15 \times 0.10 \times 0.10 \text{ mm}$

### Data collection

Rigaku AFC-5R diffractometer  
 $\omega-2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\min} = 0.656$ ,  $T_{\max} = 0.699$   
 2204 measured reflections  
 337 independent reflections  
 318 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$   
 $\theta_{\max} = 27.5^\circ$   
 $h = 0 \rightarrow 8$   
 $k = 0 \rightarrow 8$   
 $l = 0 \rightarrow 17$   
 3 standard reflections  
 every 150 reflections  
 intensity decay: 0.5%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.087$   
 $S = 1.02$   
 337 reflections  
 27 parameters  
 H-atom parameters not refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.8319P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.63 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.87 \text{ e \AA}^{-3}$   
 Extinction correction:  
 SHELXL97  
 Extinction coefficient:  
 0.0092 (18)

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Co—O3	2.064 (3)	V—O2	1.9959 (16)
Co—O1	2.157 (4)	P—O2	1.5511 (17)
V—O1	1.624 (4)		
O1—V—O2	106.05 (6)	O2 <sup>vi</sup> —P—O2 <sup>viii</sup>	111.01 (7)
O2—V—O2 <sup>iii</sup>	85.62 (3)	O2 <sup>vi</sup> —P—O2 <sup>viii</sup>	106.43 (13)
O2—V—O2 <sup>iv</sup>	147.90 (11)	P—O2—V	126.66 (11)

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

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H1 $\cdots$ O2 <sup>ix</sup>	0.83	1.98	2.803 (2)	168.9

Symmetry codes: (ix)  $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$ .

H atoms were found in a difference Fourier map and their positions were fixed at calculated positions during the refinement, with O—H distances of  $0.829 \text{ \AA}$  and a common isotropic displacement parameter [ $U_{\text{iso}}(\text{H}) = 0.05 \text{ \AA}^2$ ].

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1987); cell refinement: *TEXSAN* (Molecular Structure Corporation, 1987); data reduction: *TEXRAY* in *TEXSAN*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1416). Services for accessing these data are described at the back of the journal.

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