Acta Crystallographica Section C
**Crystal Structure
Communications**

ISSN 0108-2701

$Ba_5Cl_4(H_2O)_8(VPO_5)_8$: a novel three-dimensional framework solid

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Received 2 November 2009
Accepted 11 January 2010
Online 3 February 2010

The novel hydrothermally synthesized title compound, pentabarium tetrachloride octahydrate octakis(oxovanadium phosphate), $Ba_5Cl_4(H_2O)_8(VPO_5)_8$, crystallizes in the orthorhombic space group *Cmca* with a unit cell containing four formula units. Two Ba^{2+} cations, two Cl^- anions and the O atoms of four water molecules are situated on the (100) mirror plane, while the third independent Ba^{2+} cation is on the intersection of the (100) plane and the twofold axis parallel to *a*. Two phosphate P atoms are on twofold axes, while the remaining independent P atom and both V atoms are in general positions. The structure is characterized by two kinds of layers, namely anionic oxovanadium phosphate (VPO_5), composed of corner-sharing VO_5 square pyramids and PO_4 tetrahedra, and cationic barium chloride hydrate clusters, $Ba_5Cl_4(H_2O)_8$, composed of three Ba^{2+} cations linked by bridging chloride anions. The layers are connected by Ba—O bonds to generate a three-dimensional structure.

Comment

The V–P–O system has received considerable attention, not only because of its application to catalysis, but also due to its rich and impressive structural chemistry associated with the ability of vanadium to have tetrahedral, square-pyramidal and octahedral coordination environments in various oxidation states. The introduction of pyridinium cations into the V–P–O system leads to rather complicated structures (Huang *et al.*, 2001; Luan *et al.*, 2001). Several structures have also been reported with the introduction of organic ammonium cations into the V–P–O system (Zhang *et al.*, 1995; Soghomonian *et al.*, 1996; Luan *et al.*, 2003). A few structures with introduction of inorganic cations into the P—V—O system have also been reported (Soghomonian *et al.*, 1998; Khan *et al.*, 1996; Tian & Wu, 2002). In the present paper, we report a new compound, $Ba_5Cl_4(H_2O)_8(PVO_5)_8$, in which the oxovanadium phosphate framework is templated by an unusual cationic barium chloride hydrate cluster of composition $Ba_5Cl_4(H_2O)_8$.

$Ba_5Cl_4(H_2O)_8(VPO_5)_8$ crystallizes in the orthorhombic space group *Cmca* with a unit cell consisting of four asymmetric units. The coordination environments of the V, P and Ba atoms are shown in Fig. 1. Each of the two independent V sites in the asymmetric unit exhibits a distorted square-pyramidal [VO_5] geometry. The basal positions are defined by O-atom donors from four adjacent phosphate groups and the apical O atoms (O1 and O2) are coordinated to adjacent Ba^{2+} cations. Based on the stoichiometry of the compound and assuming normal oxidation states for Ba, Cl, P and O, the oxidation states of vanadium are V^{IV} and V^{V} in a ratio of 3:1, *i.e.* two of the eight V atoms are V^{V} and six are V^{IV}. Bond-valence sum calculations (Brese & O'Keeffe, 1991) for V1 and V2 give values of 4.42 and 4.35, respectively. The mean valence, 4.385, is reasonably close to 4.25 for V^{IV}:V^{V} = 3:1. Similar mixed bond-valence sums for V atoms have been reported in other oxovanadium phosphates (Zhang *et al.*, 1999; Le Fur *et al.*, 2001). Atoms Ba1, Ba2, Cl1, Cl2 and O11–O14 are situated on the (100) mirror plane, while atom Ba3 is on the intersection of the (100) plane and the twofold axis parallel to *a*. Atom P1 is on the twofold axis parallel to *b* and atom P3 is on the twofold axis parallel to *a*. All other atoms, *i.e.* V1, V2, P2 and O1–O10, are on general positions.

Atoms Ba1 and Ba2 are both 11-coordinate, with four phosphate O atoms, two vanadyl oxide atoms, three water molecules and two bridging chloride anions. Atom Ba3 is ten-coordinate, with four phosphate O atoms, four water molecules and two bridging chloride anions. The Ba—O bond lengths range from 2.725 (4) to 3.086 (7) Å, while the O—Ba—O angles span the range 46.77 (10)–180°. The Ba—Cl bond lengths vary from 3.225 (2) to 3.362 (2) Å, with the Cl—Ba—Cl angles in the range 131.61 (5)–180°.

There are two kinds of layer in the structure, namely anionic oxovanadium phosphate (VPO_5) and cationic barium chloride hydrate, $Ba_5Cl_4(H_2O)_8$. The VPO_5 layers consist of a checkerboard pattern of corner-sharing VO_5 square pyramids and PO_4

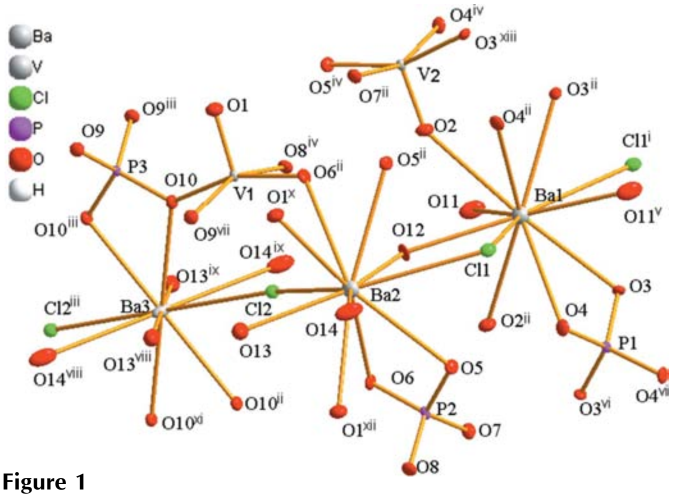

Figure 1
The asymmetric unit and the complete coordination environments of the V, Ba and P atoms in the structure of $Ba_5Cl_4(H_2O)_8(VPO_5)_8$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, y, z$; (iii) $x, -y+1, -z+1$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (v) $x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $-x+\frac{1}{2}, y, -z+\frac{1}{2}$; (vii) $-x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (viii) $x, 2-y, 1-z$; (ix) $x, -1+y, z$; (x) $-\frac{1}{2}-x, \frac{1}{2}+y, z$; (xi) $-x, 1-y, 1-z$; (xii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (xiii) $-\frac{1}{2}+x, y, \frac{1}{2}-z$.]

doi:10.1107/S0108270110001393

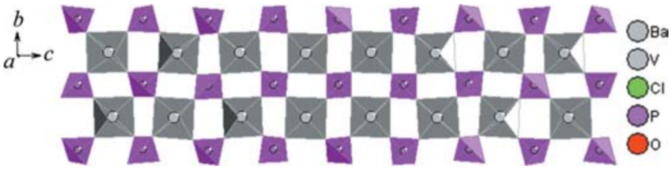

Figure 2
A view of the VPO_5 layers along the *a* axis. The VO_5 square pyramids are larger and the PO_4 tetrahedra are smaller.

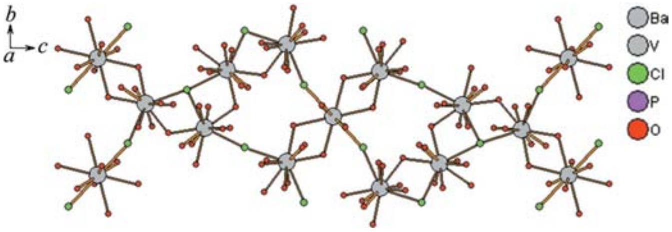

Figure 3
A view of the $Ba_5Cl_4(H_2O)_8$ layers along the *a* axis.

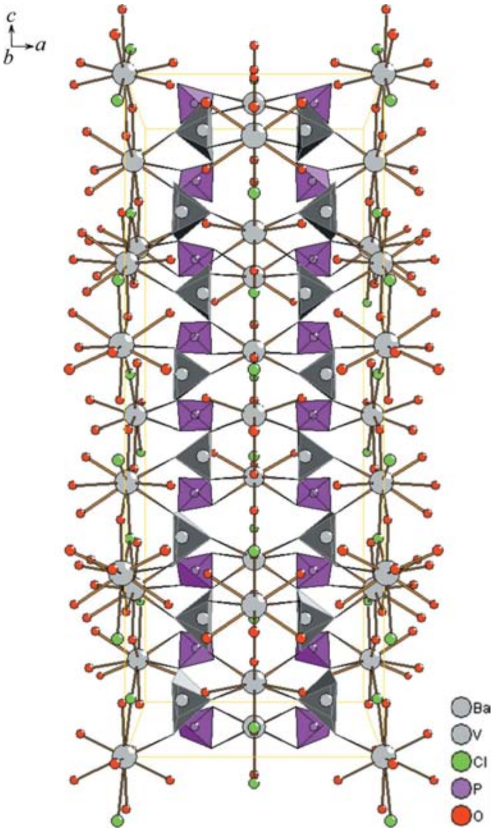

Figure 4
The three-dimensional structure of $Ba_5Cl_4(H_2O)_8(VPO_5)_8$, viewed along the *b* axis. The layers parallel to the *bc* plane can be seen to stack along the *a* axis.

tetrahedra in the *bc* plane, and are similar to those found in $Na_3V_2O_2F(PO_4)_2$ (Massa *et al.*, 2002) (Fig. 2). In the layers of barium chloride hydrate, clusters of three Ba^{2+} cations are linked *via* additional bridging of the chloride anions and water molecules to form a two-dimensional network in the *bc* plane (Fig. 3). To our knowledge, this barium chloride hydrate structural unit is unprecedented. Adjacent VPO_5 and $Ba_5Cl_4(H_2O)_8$ layers are connected by Ba—O bonds involving both phosphate and vanadyl O atoms of the anionic layers, and the layers alternate along the *a* axis to generate the three-dimensional structure (Fig. 4).

Experimental

Single crystals of the title compound were prepared from a mixture of NH_4VO_3 (2 mmol, 0.234 g), $BaCl_2$ (2 mmol, 0.4886 g), H_3BO_3 (2.5 mmol, 0.1758 g), H_3PO_4 (2 ml) and H_2O (2 ml). The mixture was sealed in a 30 ml Teflon-lined stainless steel vessel and heated at 443 K for 6 d under autogenous pressure, then cooled to room temperature. The resulting dark-green crystals were collected and dried in air at ambient temperature.

Crystal data

$Ba_5Cl_4(H_2O)_8(VPO_5)_8$
$M_r = 2267.91$
Orthorhombic, *Cmca*
$a = 13.5073$ (8) Å
$b = 8.8803$ (5) Å
$c = 35.482$ (2) Å
$V = 4256.1$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 6.90$ mm^{-1}
$T = 295$ K
$0.20 \times 0.12 \times 0.12$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
$T_{\min} = 0.339$, $T_{\max} = 0.492$
10601 measured reflections
1993 independent reflections
1614 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.078$
$S = 1.04$
1993 reflections
180 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.63$ e Å^{-3}
$\Delta\rho_{\min} = -1.20$ e Å^{-3}

The H atoms were located in a difference map and included in the model with O—H distances constrained to 0.85 Å and with $U_{\rm iso}(H) = 1.2U_{\rm eq}(O)$. The highest peak in the difference map is 1.82 Å from atom H11 and the deepest hole is 0.66 Å from atom Ba1.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); 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*.

We thank the Universities and Colleges Natural Science Foundation of Henan (grant No. 2009A150011) and the Natural Science Foundation of China (grant No. 200903036) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3227). Services for accessing these data are described at the back of the journal.

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