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A new type of mixed anionic framework in microporous rubidium copper vanadyl(V) phosphate, $Rb_2Cu(VO_2)_2(PO_4)_2$

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In dirubidium copper bis[vanadyl(V)] bis(phosphate), $Rb_2Cu(VO_2)_2(PO_4)_2$, three different oxo complexes form an anionic framework. VO_5 polyhedra in a trigonal bipyramidal configuration and PO_4 tetrahedra share vertices to form eight-membered rings, which lie in layers perpendicular to the *a* axis of the monoclinic unit cell. Cu atoms at centres of symmetry have square-planar coordination and link these layers along [100] to form a three-dimensional anionic framework, *viz.* $[Cu(VO_2)_2(PO_4)_2]^{2-}_{\infty}$. Intersecting channels in the [100], [001] and [011] directions contain Rb^+ cations. Topological relations between this new structure type and the crystal structures of $A(VO_2)(PO_4)$ (A = Ba, Sr or Pb) and $BaCrF_2LiF_4$ are discussed.

Comment

The rich chemistry of vanadium includes a range of coordination geometries with oxygen in crystal structures which include tetrahedral, pentahedral, trigonal pyramidal, tetragonal pyramidal and octahedral. Combined with its variable oxidation states of 2, 3, 4 and 5, this leads to a large diversity of vanadium-containing structures. The amphoteric character of vanadium oxo complexes explains the peculiarities of its crystal chemistry: these oxo complexes can have both cation- and anion-forming functions in mineral and biological processes (Baran, 2003). As a cation (V^{3+}, VO^{2+}, VO_2^{+}), vanadium acts like a typical transition metal, while its anionic form (VO_4^{3-}) resembles phosphorous in phosphates. In spite of the fact that phosphate and vanadate minerals often have isotypic crystal structures, there are no cases of isomorphous substitution between VO_4 and PO_4 tetrahedra, most certainly due to the large difference in the sizes of V^{5+} and P^{5+} ions. However, a solid solution between VO_4 and AsO_4 is known, as found in the crystal structure of the volcanic mineral coparsite, $Cu_4ClO_2[(As_{0.5}V_{0.5})O_4]$ (Starova *et al.*, 1998).

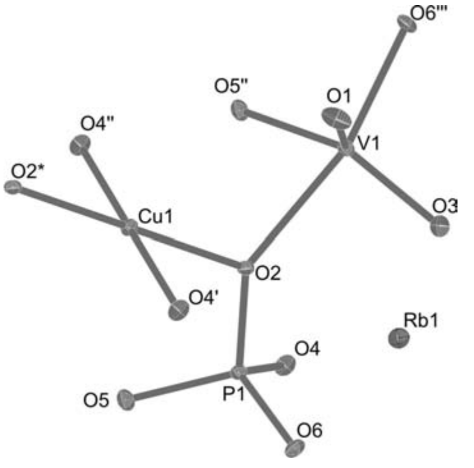

Figure 1
The main structural elements of the title compound, showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 70% probability level. [Symmetry codes: (*) $1 - x, 1 - y, 1 - z$; (′) $1 + x, y, z$; (″) $-x, 1 - y, 1 - z$; (‴) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.]

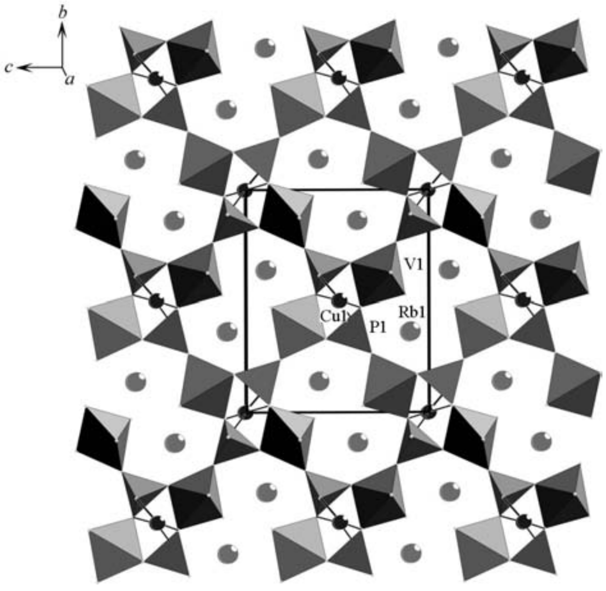

Figure 2
The $Rb_2Cu(VO_2)_2(PO_4)_2$ crystal structure in the [100] projection.

Mineral and synthetic phases with complex anions and open framework structures have been intensively studied over the last two decades. Among them, vanadyl phosphates seem to be promising due to their potential applications as catalytic materials, sorbents, molecular sieves or ion-exchange materials similar to zeolites (Centi *et al.*, 1988). As part of our investigation of these types of compounds (Massa *et al.*, 2002; Yakubovich *et al.*, 2006), we present here the title compound, which has a microporous structure with an open mixed framework formed by Cu, V and P oxo complexes.

The V^{5+} ions in the structure (Fig. 1) occupy strongly distorted five-vertex VO_5 polyhedra. The two shortest V1—O

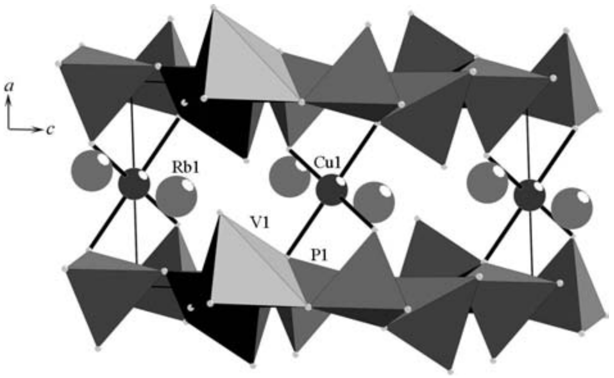

Figure 3
Layers of VO_5 bipyramids and PO_4 tetrahedra linked by Cu atoms to form a three-dimensional anionic framework in the $Rb_2Cu(VO_2)_2(PO_4)_2$ crystal structure.

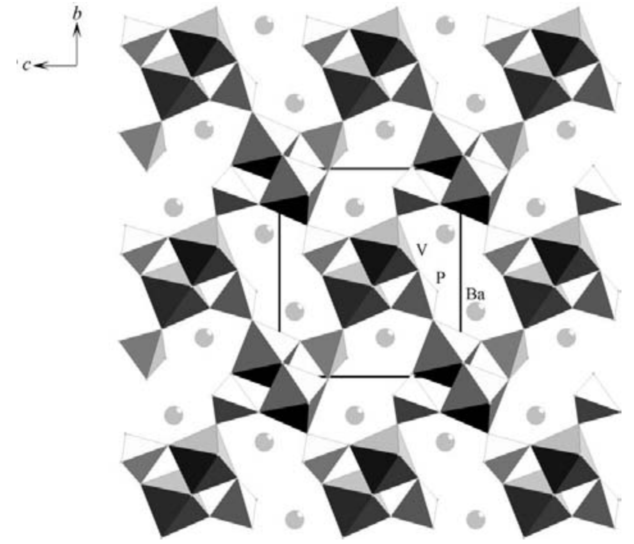

Figure 4
The layer formed by VO_6 octahedra and PO_4 tetrahedra in the $Ba(VO_2)$-(PO_4) crystal structure.

bonds (Table 1) are typical of vanadyl groups, while the three longer V1—O distances correspond to V1—O bonds where the O atoms belong to PO_4 tetrahedra. The Cu1—O distances around the square-planar Cu^{2+} cation at the centre of symmetry are 1.9072 (17) and 1.9752 (16) Å. The largest cation–oxygen distances around V1, Cu1 and P1 involve atom O2, which is shared by three polyhedra (the so-called 'loop configuration'). The VO_5 polyhedra approach a trigonal bipyramidal configuration and, together with the PO_4 tetrahedra, form mixed anionic layers parallel to the *bc* plane at $x = 0$ (Fig. 2). Alternating vertex-sharing VO_5 bipyramids and PO_4 tetrahedra form both four- and eight-membered rings within these layers. The vanadyl groups (V═O) are terminal. V1═O1 is parallel to the *a* axis, with atom O1 pointing into the inter-layer space, and V1═O3 is parallel to the *c* axis, with atom O3 pointing into the eight-membered ring. Along the [100] direction, V/P layers alternate with layers of Rb and Cu atoms at $x = 0.5$ (Fig. 3), and CuO_4 quadrilaterals link the V/P layers by sharing two vertices (O4) with P1 tetrahedra and two others (O2) with P1 and V1 polyhedra. Thus, a three-dimensional anionic framework with the formula $[Cu(VO_2)_2(PO_4)_2]^{2-}$ is formed. It contains channels with eight polyhedra at the circumference, as viewed along the [100] direction. Crossing channels are present in the [001] and [011] directions. The Rb atoms reside in these channels and are surrounded by ten O atoms, with Rb1—O distances ranging from 2.8427 (18) to 3.2981 (19) Å (average 3.108 Å) (Table 1); an additional atom $O6^i$ [symmetry code (i) as shown in Table 1] is 3.5044 (17) Å from atom Rb1. Including this 11th O atom in the first coordination sphere around Rb1 gives the wrong bond-valence sum for atom O6. Bond-valence sum data, shown in Table 2, are consistent with the assumed oxidation states of V and Cu.

In crystals of vanadyl phosphates, $[VO_2]^+$ cations in combination with PO_4^{3-} tetrahedra usually form one- (ribbons), two- (layers) or three-dimensional (framework) anions. Six different structure types based on mixed anionic one-dimensional ribbons formed by VO_5 (or VO_6) and PO_4 polyhedra have been described: $A(VO_2)(HPO_4)$, with A = K, Rb, NH_4 or Tl (Amoros *et al.*, 1988; Huan *et al.*, 1991); the α-modification of $(NH_4)(VO_2)(HPO_4)$ (Amoros & Le Bail, 1992); $A_2(VO_2)(PO_4)$, with A = K or Na (Korthuis *et al.*, 1993*a*); $K_3(VO_2)_2(PO_4)(HPO_4)(H_2O)$ (Leclaire *et al.*, 2002); $Ba_2(VO_2)(PO_4)(HPO_4)(H_2O)$ (Bircsak & Harrison, 1998*a*) and $Cd(VO_2)(PO_4)(H_2O)$ (Leclaire *et al.*, 2000). Among the two-dimensional layered structures, four different types can be distinguished: $K(VO_2)_2(PO_4)$ (Berrah *et al.*, 1999); $A(VO_2)(PO_4)$, with A = Ba, Sr or Pb (Kang *et al.*, 1992; Borel *et al.*, 2000); $Ag_2(VO_2)(PO_4)$ (Kang *et al.*, 1993) and $(CN_3H_6)_2(VO_2)_3(PO_4)(HPO_4)$ (Bircsak & Harrison, 1998*b*). Three-dimensional mixed-anionic frameworks are represented by

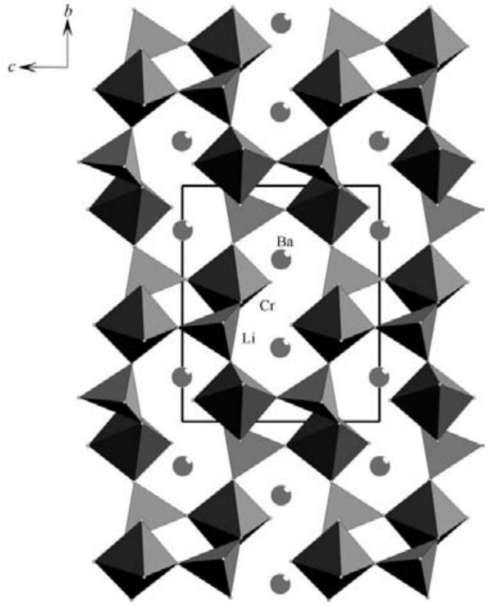

Figure 5
The three-dimensional microporous framework of CrF_6 octahedra and LiF_4 tetrahedra, with Ba atoms in channels, in the crystal structure of $BaCrLiF_6$.

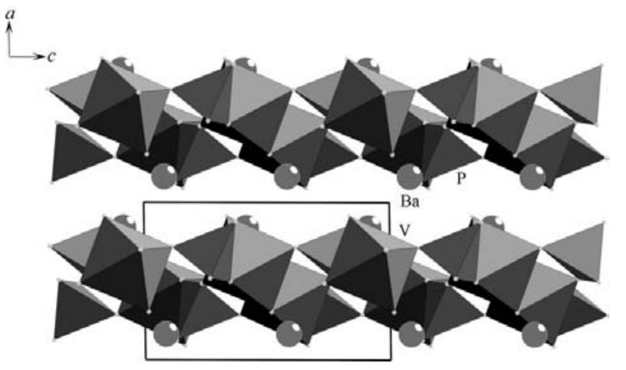

Figure 6
Double layers of VO_6 and PO_4 polyhedra in the $Ba(VO_2)(PO_4)$ crystal structure, viewed along the [010] direction.

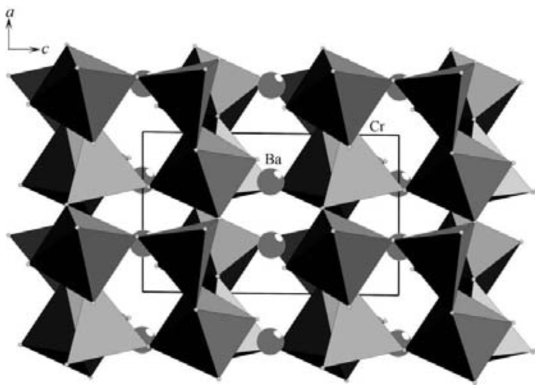

Figure 7
The $BaCrLiF_6$ crystal structure in an [010] projection.

the crystal structures of $(NH_4)(VO_2)_2(PO_4)(H_2O)_3$ (Wilde *et al.*, 2000), $Pb(VO_2)_2(PO_4)$ (Borel *et al.*, 2000) and $Pb(VO_2)(PO_4)(H_2O)$ (Leclaire *et al.*, 2001).

Sometimes, additional cations along with $[VO_2]^+$ may form three-dimensional mixed-anionic frameworks in combination with PO_4 tetrahedra. Two compounds of this kind include $Cs_2[(UO_2)(VO_2)_2(PO_4)_2]\cdot 0.59H_2O$ (Shvareva *et al.*, 2005) and $Cs_2[Ti(VO_2)_3(PO_4)_3]$ (Yakubovich *et al.*, 2006). The novel crystal structure of $Rb_2Cu(VO_2)_2(PO_4)_2$ described here belongs to this same group of vanadyl(V) phosphates having three different oxo complexes in the anionic part of their structures.

To our knowledge, only one crystal structure among the vanadyl phosphates published so far contains $[VO_2]^+$ ions participating in the formation of the cationic framework. There is a close-packed framework formed by edge-sharing LiO_6 and VO_6 octahedra in $[Li_2(VO_2)](PO_4)$ (Korthuis *et al.*, 1993*b*). This crystal structure is based on hexagonal close-packing of O atoms, in which Li and V atoms occupy octahedral voids and a fraction of the tetrahedral voids contain P atoms.

The novel crystal structure of rubidium copper vanadyl phosphate is closely related to the structures of $A(VO_2)(PO_4)$, with A = Ba, Sr or Pb (Kang *et al.*, 1992; Borel *et al.*, 2000), and $BaCrF_2LiF_4$ (Babel, 1974), in having similar unit-cell parameters and the same space group, $P2_1/c$ (Table 3). In *bc* projections of the $Ba(VO_2)(PO_4)$ and $Ba(CrF_2)(LiF_4)$ crystal structures (Figs. 4 and 5), one can see eight-membered windows formed by alternating octahedra (VO_6 and CrF_6) and tetrahedra (PO_4 and LiF_4) sharing vertices. These windows are topologically very similar to the windows walled in by VO_5 bipyramids and PO_4 tetrahedra in the title structure (Fig. 2). In all three structures, the eight-membered windows enclose large channels parallel to the [100] direction which contain Rb, Ba, Sr or Pb atoms. The main topological difference between these structures occurs along the *a* axis of their monoclinic unit cells. In the V/P layers of rubidium copper vanadyl phosphate, V bipyramids have no O atoms shared between them. Cu atoms with square-planar coordination link these V/P layers along the *a* axis to form the three-dimensional mixed anionic framework (Fig. 3). Sharing one vertex between two neighbouring V octahedra in barium vanadyl phosphate leads to the formation of double V/P layers alternating with Ba ions along [100] (Fig. 6). In the $Ba(CrF_2)(LiF_4)$ structure, eight-membered ring layers are linked along the *a* axis through common vertices of Cr octahedra and Li tetrahedra, resulting in the three-dimensional structure (Fig. 7).

Experimental

Light-blue plate-shaped crystals of $Rb_2Cu(VO_2)_2(PO_4)_2$ up to 0.5 mm long were formed by hydrothermal synthesis in the $CuCl_2$–Rb_3PO_4–V_2O_5–H_2O system (weight ratio 1:6:3:30) in a PTFE-lined stainless steel autoclave (temperature = 553 K and pressure = 7×10^3 kPa) over a period of 20 d. The presence of Rb, Cu, V and P in the samples was confirmed by qualitative X-ray spectroscopic analysis.

Crystal data

$Rb_2Cu(VO_2)_2(PO_4)_2$
M_r = 590.31
Monoclinic, $P2_1/c$
a = 4.9292 (9) Å
b = 11.471 (2) Å
c = 9.4810 (17) Å
β = 93.535 (3)°
V = 535.04 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 13.08 mm^{-1}
T = 100 (2) K
0.20 × 0.08 × 0.04 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min}$ = 0.285, $T_{\max}$ = 0.600
6107 measured reflections
1290 independent reflections
1221 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.048
S = 1.14
1290 reflections
89 parameters
$\Delta\rho_{\max}$ = 0.52 e Å^{-3}
$\Delta\rho_{\min}$ = −0.51 e Å^{-3}

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Table 1
Selected geometric parameters (Å, °).

Rb1—O5^{i}	2.8427 (18)	V1—O1	1.6209 (19)
Rb1—O4^{ii}	2.9436 (18)	V1—O6^{vi}	1.9435 (17)
Rb1—O3^{ii}	2.9619 (18)	V1—O5^{vii}	1.9855 (18)
Rb1—O6	3.0066 (17)	V1—O2	2.0901 (17)
Rb1—O3^{iii}	3.0288 (18)	P1—O4	1.5225 (18)
Rb1—O1	3.2266 (19)	P1—O6	1.5225 (17)
Rb1—O1^{iv}	3.228 (2)	P1—O5	1.5401 (18)
Rb1—O2	3.2537 (17)	P1—O2	1.5670 (18)
Rb1—O3	3.2910 (18)	Cu1—O4^{ii}	1.9072 (17)
Rb1—O1^{v}	3.2981 (19)	Cu1—O2	1.9752 (16)
V1—O3	1.6204 (18)		
O3—V1—O1	108.86 (10)	O6—P1—O5	109.67 (10)
O3—V1—O6^{vi}	100.69 (8)	O4—P1—O2	110.60 (9)
O1—V1—O6^{vi}	98.27 (8)	O6—P1—O2	106.64 (10)
O3—V1—O5^{vii}	129.13 (8)	O5—P1—O2	106.43 (10)
O1—V1—O5^{vii}	121.09 (9)	O4^{vii}—Cu1—O2	89.90 (7)
O6^{vi}—V1—O5^{vii}	82.01 (7)	O4^{ii}—Cu1—O2	90.10 (7)
O3—V1—O2	91.49 (8)	P1—O5—V1^{vii}	130.65 (10)
O1—V1—O2	88.75 (8)	P1—O4—Cu1^{viii}	125.25 (10)
O6^{vi}—V1—O2	163.05 (7)	P1—O6—V1^{ix}	139.73 (11)
O5^{vii}—V1—O2	81.15 (7)	P1—O2—Cu1	117.19 (10)
O4—P1—O6	111.15 (10)	P1—O2—V1	128.68 (10)
O4—P1—O5	112.10 (10)		

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

Table 2
Bond-valence data (Pyatenko, 1972).

	V1	Cu1	P1	Rb1	Σ
O1	1.636			0.089, 0.089, 0.086	1.900
O2	0.460	0.447	1.086	0.088	2.081
O3	1.654			0.111, 0.106, 0.086	1.957
O4		0.553	1.338	0.113	2.004
O5	0.588		1.237	0.123	1.948
O6	0.662		1.338	0.108	2.108
Σ	5.000	2.000	4.999	0.999	

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3147). Services for accessing these data are described at the back of the journal.

Table 3
Crystal data for $Rb_{0.5}Cu(VO_2)(PO_4)$, $Ba(VO_2)(PO_4)$ and $Ba(CrF_2)(LiF_4)$ (space group $P2_1/c$, $Z = 4$).

	$Rb_{0.5}Cu(VO_2)(PO_4)$	$Ba(VO_2)(PO_4)$	$Ba(CrF_2)(LiF_4)$
Unit-cell parameters			
a (Å)	4.9292 (9)	5.616 (2)	5.397 (3)
b (Å)	11.471 (2)	10.062 (1)	10.355 (5)
c (Å)	9.4810 (17)	8.727 (1)	8.638 (5)
β (°)	93.535 (3)	90.90 (2)	90.72 (5)
V (Å^3)	535.04	493.09	482.7
ρ_{calc} (Mg m^{-3})	3.67	4.25	4.27
Tetrahedron composition	PO_4	PO_4	LiF_4
Pentahedron/octahedron composition	VO_5	VO_6	CrF_6
Reference	Present work	Kang *et al.* (1992)	Babel (1974)

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