within 3 h. The resulting melt was washed with dimethylformamide and the residue was dried *in vacuo*.

Crystal data

KCu_4Se_3
$M_r = 530.14$
Tetragonal
$P4/mmm$
$a = 4.0188\,(3)$ Å
$c = 9.7200\,(10)$ Å
$V = 156.99\,(2)$ Å^3
$Z = 1$
$D_x = 5.608$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 82 reflections
$\theta = 11.0–22.5°$
$\mu = 31.277$ mm^{-1}
$T = 293\,(2)$ K
Plate
$0.07 \times 0.06 \times 0.02$ mm
Black

Data collection

Stoe AED-II four-circle diffractometer
ω/θ scans
Absorption correction: analytical (*XP* in *SHELXTL/PC*; Siemens, 1990)
$T_{\min} = 0.223$, $T_{\max} = 0.535$
1026 measured reflections
174 independent reflections
160 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\max} = 29.93°$
$h = 0 \rightarrow 5$
$k = -5 \rightarrow 5$
$l = -13 \rightarrow 13$
4 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 1.170$
174 reflections
13 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.839$ e Å^{-3}
$\Delta\rho_{\min} = -1.002$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.07 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0	1/2	0.16146 (8)	0.0238 (3)
Se1	1/2	1/2	0	0.0139 (3)
Se2	0	0	0.30109 (7)	0.0143 (3)
K	1/2	1/2	1/2	0.0210 (5)

Table 2. *Selected geometric parameters (Å, °)*

Cu—Se2	2.4248 (6)	Cu—Cu$^{\rm i}$	2.8417 (2)
Cu—Se1	2.5497 (5)	Se2—K	3.4371 (4)
Se2$^{\rm ii}$—Cu—Se2	111.93 (4)	Se1$^{\rm iii}$—Cu—Se1	104.02 (3)
Se2—Cu—Se1$^{\rm iii}$	110.152 (8)		

Symmetry codes: (i) $-y, x, z$; (ii) $x, 1 + y, z$; (iii) $x - 1, y, z$.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

This work is supported by the state of Schleswig–Holstein.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1247). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 288–291

A new vanadium(IV) monophosphate, $Sr(VO)_2(PO_4)_2$, isotypic with $Ca(VO)_2(PO_4)_2$

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(Received 4 June 1998; accepted 28 September 1998)

Abstract

A new vanadium(IV) phosphate, namely, strontium bis[oxovanadium(IV)] bis(phosphate), $Sr(VO)_2(PO_4)_2$, has been synthesized. It crystallizes in the *Fdd*2 space group with $a = 11.992\,(3)$, $b = 15.932\,(2)$ and $c = 7.222\,(2)$ Å. This new phase is isostructural with $Ca(VO)_2(PO_4)_2$ and $Cd(VO)_2(PO_4)_2$ (orthorhombic form). The three-dimensional framework consists of infinite $[VO_3]_\infty$

chains linked through PO_4 tetrahedra. In the $[VO_3]_\infty$ chains, the VO_6 octahedra share their corners. This framework delimits intersecting tunnels, where the Sr^{2+} cations are located. The presence of V^{4+} is confirmed by thermogravimetric analysis and magnetic susceptibility measurements.

Comment

The $[V_2P_2O_{10}]_\infty$ host lattice consists of corner-sharing octahedra and PO_4 tetrahedra. Three sorts of tunnel run along [100], [001] and [110], where the Sr^{2+} cations are located (Fig. 1).

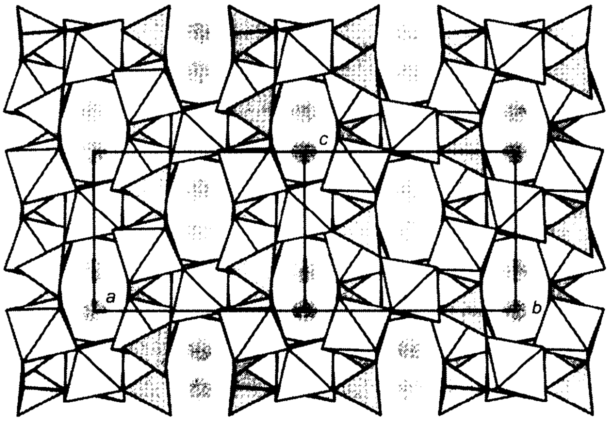

Fig. 1. Projection of the structure along [110].

The title structure consists of identical $[VPO_7]_\infty$ layers parallel to (010), built up of $[VO_3]_\infty$ chains of corner-sharing VO_6 octahedra. In each $[VPO_7]_\infty$ layer, the $[VO_3]_\infty$ chains are linked through PO_4 tetrahedra. In fact, two successive layers are oriented differently, *i.e.* they are deduced from each other by a binary axis, so that the $[VO_3]_\infty$ chains of two successive layers run along the [101] and [10$\bar{1}$] directions. In this framework, each PO_4 tetrahedron shares two apices with two $[VO_3]_\infty$ chains of its $[VPO_7]_\infty$ layer, and two apices with two successive octahedra of one $[VO_3]_\infty$ chain of the adjacent $[VPO_7]_\infty$ layer. The interatomic distances observed for this compound show great similarity with the two isotypes $Ca(VO)_2(PO_4)_2$ (Lii *et al.*, 1992) and $Cd(VO)_2(PO_4)_2$ (Leclaire *et al.*, 1993). In the PO_4 tetrahedra, the P—O bond lengths (range 1.51–1.56 Å) are very close to those observed for both calcium phosphate (range 1.53–1.55 Å) and cadmium phosphate (range 1.52–1.55 Å). In the same way, the distorted geometry of the VO_6 octahedron is very similar in the three compounds. This geometry involves one short bond of 1.62 Å (1.60 Å for Ca and Cd), four intermediate distances ranging from 2.01 to 2.07 Å (2.02–2.06 Å for Ca and 2.00–2.05 Å for Cd) and one long distance of 2.13 Å opposite the short one (2.12 Å for Ca and 2.09 Å for Cd).

The strontium coordination is very similar to that shown previously by the Ca and Cd structures. The Sr^{2+} cation forms a rhombic prism, with Sr—O distances ranging from 2.45 to 2.73 Å (2.41–2.67 Å for Ca and 2.32–2.70 Å for Cd).

Calculation of the bond valence sum of the atoms using the Brese & O'Keeffe (1991) formulation leads to a valence state of 3.93 for vanadium. The tetravalent vanadium is confirmed by the $\chi^{-1}(T)$ curve (Fig. 2), which leads to an effective magnetic moment of 1.66 μ_B per vanadium, in good agreement with the theoretical value of 1.73 μ_B for V^{IV}. The thermogravimetric analysis in air also shows an increase in weight (observed 3.2%) corresponding to the complete oxidation of V^{IV} to V^{V} (theoretical 3.9%).

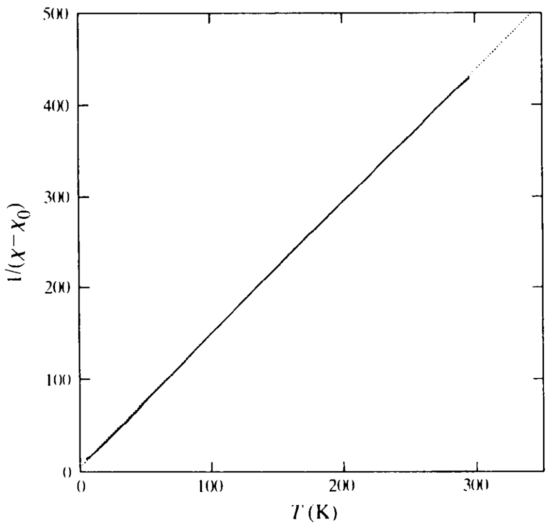

Fig. 2. The inverse molar susceptibility *versus* T (K).

The cell volume of the isotypic compounds increases from Cd^{2+} to Sr^{2+} to Ca^{2+}, in agreement with the 'effective ionic radii' of the interpolated cations (1311.5/1.10, 1338.5/1.12 and 1379.8 Å^3/1.26 Å, respectively).

Experimental

Single crystals of $Sr(VO)_2(PO_4)_2$ were obtained initially during a study of the Sr–V–Mo–P–O system from a mixture of nominal composition $SrVMo_2P_2O_{14}$. The growth was carried out in two steps. Firstly, $H(NH_4)_2PO_4$, $SrCO_3$ and MoO_3 were mixed in an agate mortar in adequate ratios according to the composition $SrMo_{1.83}P_2O_{11.5}$ and heated at 672 K in a platinum crucible to decompose the ammonium phosphate and the carbonate. In a second step, the resulting mixture was added to molybdenum (0.135 mol) and V_2O_5 (0.5 mol), then sealed in an evacuated silica ampoule and heated for one day at

1100 K and cooled at 1.3 K h^{-1} to 800 K and finally quenched to room temperature. Two sorts of crystal were extracted from the resulting mixture, *i.e.* colorless crystals identified as MoO_3 and dark-green crystals. The latter were studied by X-ray diffraction and microprobe analysis, confirming both the composition $SrV_2P_2O_{10}$ deduced from the structure determination and the absence of molybdenum. The synthesis of a powder of this new phase was carried out under similar experimental conditions. In the first step, $H(NH_4)_2PO_4$ and $SrCO_3$ were mixed according to the composition SrP_2O_6, and in the second step, the mixture was added to VO_2 (2 mol), sealed in an evacuated silica ampoule, heated at 1100 K for one day, cooled at 8.3 K h^{-1} to 873 K and finally quenched to room temperature. Under these conditions, a single phase was obtained in the form of a pale-green polycrystalline sample whose powder X-ray diffraction pattern was indexed in an orthorhombic cell with the parameters deduced from the single-crystal X-ray study.

Crystal data

$Sr(VO)_2(PO_4)_2$
$M_r = 411.45$
Orthorhombic
*Fdd*2
$a = 11.992(3)$ Å
$b = 15.932(2)$ Å
$c = 7.222(2)$ Å
$V = 1379.8(5)$ Å^3
$Z = 8$
$D_x = 3.96$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18\text{–}22°$
$\mu = 10.87$ mm^{-1}
$T = 293$ K
Needle
0.114 × 0.062 × 0.048 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
Bisecting scans
Absorption correction: Gaussian (*ABSORB* in *Xtal*3.2; Hall *et al.*, 1992)
$T_{min} = 0.494$, $T_{max} = 0.593$
1581 measured reflections
1581 independent reflections

747 reflections with $I > 3\sigma(I)$
$\theta_{max} = 44.87°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 30$
$l = 0 \rightarrow 14$
3 standard reflections frequency: 60 min intensity decay: 0.3%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.041$
$S = 2.454$
747 reflections
68 parameters
Weighting scheme based on measured s.u.'s; $w = 1/\sigma^2$

$(\Delta/\sigma)_{max} = 0.0004$
$\Delta\rho_{max} = 2.36$ e Å^{-3}
$\Delta\rho_{min} = -1.99$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sr	0	0	0	0.0079 (4)
V	0.1389 (1)	0.13140 (8)	0.6477 (3)	0.0076 (5)
P	0.2496 (3)	0.04084 (9)	0.2586 (6)	0.0056 (7)
O1	0.2466 (6)	0.1675 (2)	0.759 (1)	0.006 (2)
O2	0.1042 (6)	0.2341 (4)	0.497 (1)	0.007 (3)
O3	0.2388 (5)	0.0981 (4)	0.425 (1)	0.009 (3)
O4	0.1478 (6)	0.0168 (4)	0.769 (1)	0.007 (3)
O5	0.0131 (5)	0.1516 (5)	0.835 (1)	0.010 (3)

Table 2. *Selected geometric parameters (Å, °)*

Sr—O4^{i}	2.447 (8)	V—O2	2.011 (7)
Sr—O5^{i}	2.696 (8)	V—O3	2.073 (8)
Sr—O4^{ii}	2.447 (8)	V—O4	2.029 (6)
Sr—O5^{ii}	2.696 (8)	V—O5	2.054 (8)
Sr—O2^{iii}	2.508 (8)	V—O1^{iv}	2.129 (8)
Sr—O3^{iii}	2.734 (7)	P—O3	1.516 (9)
Sr—O2^{iv}	2.508 (8)	P—O4^{v}	1.537 (7)
Sr—O3^{iv}	2.734 (7)	P—O2^{iii}	1.541 (7)
V—O1	1.624 (8)	P—O5^{vi}	1.559 (9)
O1—V—O2	98.3 (3)	O3—V—O1^{iv}	90.2 (3)
O1—V—O3	90.8 (4)	O4—V—O5	83.9 (3)
O1—V—O4	93.7 (3)	O4—V—O1^{iv}	85.2 (3)
O1—V—O5	101.7 (4)	O5—V—O1^{iv}	77.3 (3)
O1—V—O1^{iv}	178.6 (4)	O3—P—O4^{v}	112.9 (4)
O2—V—O3	84.7 (3)	O3—P—O2^{iii}	109.2 (4)
O2—V—O4	168.0 (3)	O3—P—O5^{vi}	106.9 (4)
O2—V—O5	94.5 (3)	O4^{v}—P—O2^{iii}	107.4 (3)
O2—V—O1^{iv}	82.8 (3)	O4^{v}—P—O5^{vi}	108.0 (4)
O3—V—O4	94.3 (3)	O2^{iii}—P—O5^{vi}	112.6 (4)
O3—V—O5	167.5 (3)	V—O1—V^{vii}	137.8 (2)

Symmetry codes: (i) $x, y, z-1$; (ii) $-x, -y, z-1$; (iii) $\frac{1}{4}-x, y-\frac{1}{4}, z-\frac{1}{4}$; (iv) $x-\frac{1}{4}, \frac{1}{4}-y, z-\frac{1}{4}$; (v) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (vi) $\frac{1}{4}+x, \frac{1}{4}-y, z-\frac{3}{4}$; (vii) $\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z$.

Single crystals were first selected optically and then tested by the Weissenberg method which also shows the *mmm* Laue symmetry. The systematic extinctions $h+k \neq 2n$, $k+l \neq 2n$, $h+l \neq 2n$ for hkl, and $k+l \neq 4n$ for $0kl$, $h+l \neq 4n$ for $h0l$ are characteristic of the *Fdd*2 space group. The structure was solved using the atomic coordinates of the isotypic compound $Cd(VO)_2(PO_4)_2$ (Leclaire *et al.*, 1993), similar to $Ca(VO)_2(PO_4)_2$ (Lii *et al.*, 1992). All calculations were performed on a SPARK station with the *Xtal*3.2 package (Hall *et al.*, 1992). The coordinates and atom numbering were chosen to be coherent with the other phosphates studied and to have the asymmetric unit in the center of the cell with positive coordinates. The magnetic susceptibility was measured with a Quantum Design SQUID magnetometer from 4.5 to 300 K. The inverse molar susceptibility $[\chi_m^{-1}(T)]$, established after correction of the sample holder signal, has been fitted with a Curie–Weiss law $[\chi_m = \chi_0 + C_m/(T-\theta)]$. The microgravimetric analysis was performed in oxygen using a SETARAM microbalance, heating the sample to 1073 K at a speed of 150 K h^{-1}.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.2. Program(s) used to solve structure: *Xtal*3.2. Program(s) used to refine structure: *CRYLSQ* in *Xtal*3.2. Molecular graphics: *ATOMS* (Dowty, 1995). Software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.2.

The authors thank Dr J. Provost for the investigation of the magnetic susceptibilities of their samples.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1016). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C55, 291–293

$Ca_2(H_3O)_2[V_{10}O_{28}]\cdot 16H_2O$

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(*Received 3 June 1998; accepted 15 October 1998*)

Abstract

The crystal structure of dicalcium bis(oxonium) decavanadate hexadecahydrate has been determined by X-ray analysis. The main feature of the structure is the $[V_{10}O_{28}]^{6-}$ anion, built up from ten distorted edge-sharing VO_6 octahedra with well established structures. Each Ca^{2+} ion is surrounded by seven water molecules in the form of a distorted pentagonal bipyramid. Water H atoms, as well as those of the H_3O^+ ions, participate in a complicated three-dimensional hydrogen-bonding system.

Comment

The $[V_{10}O_{28}]^{6-}$ decavanadate anion is one of the most investigated polyoxoanions of vanadium. The first identified salt, *i.e.* that of barium, $Ba_3[V_{10}O_{28}]\cdot 19H_2O$ (Norblad, 1875), was followed by others with alkaline, earth-alkaline and ammonium cations, for example, $Na_6[V_{10}O_{28}]\cdot 18H_2O$ (Durif *et al.*, 1980), $Ca_3[V_{10}O_{28}]\cdot 17H_2O$ (Swallow *et al.*, 1966), $Sr_3[V_{10}O_{28}]\cdot 22H_2O$ (Nieto *et al.*, 1993) and $Ba_3[V_{10}O_{28}]\cdot 19H_2O$ (Kamenar *et al.*, 1996), and by double salts such as $K_2Zn_2[V_{10}O_{28}]\cdot 16H_2O$ (Evans, 1966), $K_2Mg_2[V_{10}O_{28}]\cdot 16H_2O$, $Rb_2Mg_2[V_{10}O_{28}]\cdot 16H_2O$ and $(NH_4)_2Mg_2[V_{10}O_{28}]\cdot 16H_2O$ (Avtamonova *et al.*, 1990). It is interesting to note that the decavanadates are the only polyoxometallates found as minerals, *e.g.* $K_2Mg_2[V_{10}O_{28}]\cdot 16H_2O$ is the mineral hummerite (Weeks *et al.*, 1951), which usually occurs together with pascoite, $Ca_3[V_{10}O_{28}]\cdot 17H_2O$.

As part of our research on vanadates, molybdates and mixed molybdovanadates, the title compound, $Ca_2(H_3O)_2[V_{10}O_{28}]\cdot 16H_2O$, was prepared and studied. The centrosymmetrical decavanadate anion in this structure (Fig. 1) is built up of ten distorted VO_6 edge-sharing octahedra and is best described as a cubic close-packing of oxygen ions, with the octahedral holes filled by vanadium ions. Each VO_6 octahedron is considerably distorted, with bond angles at the V atoms ranging from 74.25 (5) to 106.46 (7)°. Accordingly, each vanadium ion is displaced from the centre of the polyhedron towards the exterior of the polyanion, causing variation of the V—O distances in the wide range 1.60–2.32 Å. The V—O distance depends upon the type of oxo ligand: $V{=}O_t$ bond lengths to the terminal oxo O atoms vary from 1.6026 (17) to 1.6167 (16) Å, $V{-}O_{2b}$ bond lengths to the O atoms bridging two V atoms vary from 1.6889 (15) to 2.0561 (16) Å, $V{-}O_{3b}$ bond lengths to the O atoms bridging three V atoms vary from 1.9128 (14) to 2.0127 (15) Å and $V{-}O_{6b}$ bond lengths to the O atoms shared between six V atoms range from 2.1100 (14) to 2.3219 (14) Å.

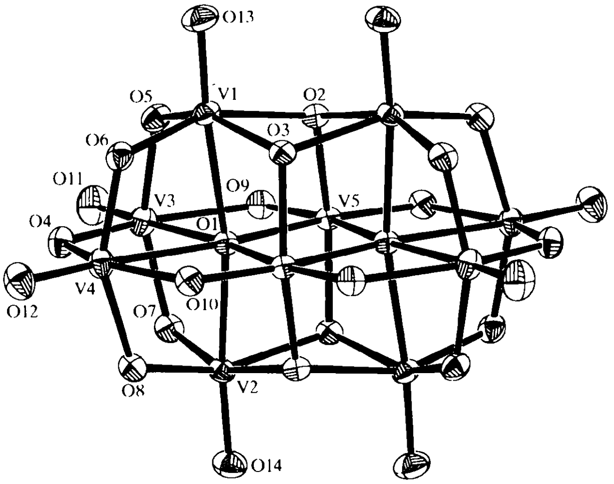

Fig. 1. The structure of the $[V_{10}O_{28}]^{6-}$ anion in $Ca_2(H_3O)_2[V_{10}O_{28}]\cdot 16H_2O$. Displacement ellipsoids are drawn at the 50% probability level.

The decavanadate anions are interconnected with calcium and hydronium cations and water molecules. The Ca^{2+} ions are surrounded by seven water molecules in a distorted pentagonal bipyramidal arrangement, with distances ranging from 2.329 (2) to 2.475 (2) Å. The hydronium ion is hydrogen bonded to three O atoms from three different decavanadate anions, with O···O