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A Mixed Valent Vanadium Phosphate Closely Related to $BaV_2P_2O_{10}$: $AgV_2P_2O_{10}$

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The structure of the mixed valent phosphate $AgV_2P_2O_{10}$ has been determined from a single crystal X-ray study. It crystallizes in the space group $P2_1/c$ with $a = 5.256(1)$ Å, $b = 8.117(1)$ Å, $c = 16.966(1)$ Å, $\beta = 91.46(1)°$. The $[V_2P_2O_{10}]_\infty$ framework derives from that of $BaV_2P_2O_{10}$ by a strong displacement of one kind of oxygen atom, leading to the formation of V_2O_{10} units of edge-sharing octahedra, instead of VO_5 pyramids. This tunnel structure is described in terms of octahedral strings $[V_4O_{20}]$ built up from corner-sharing VO_6 octahedra and V_2O_{10} units, linked through PO_4 monophosphate groups. V(IV) sits in V_2O_{10} units, whereas V(V) occupies the "isolated octahedra" according to bond valence calculations. © 1993 Academic Press, Inc.

Introduction

The studies carried out these last years in vanadium phosphates have shown the rich chemistry of these compounds, due to the ability of vanadium to exhibit two sorts of coordinations, pyramidal and octahedral. Indeed in V(V) phosphates, vanadium adopts mainly an octahedral coordination as for example in α- or β-VPO_5 (*1, 2*), whereas V(IV) can exhibit either a pure pyramidal coordination as in $Na_5V_2P_3O_{14} \cdot H_2O$ (*3*), or an octahedral coordination as in $KVPO_5$ (*4*), $NaVPO_5$ (*5, 6*), and $V_2P_2O_9$ (*7*). In fact the great flexibility of these frameworks comes from the fact that the vanadium atom generally forms an abnormally short V–O bond with one of the oxygen atom of these polyhedra, leading to a vanadyl ion. This is especially the case of $V^{IV}O_6$ octahedra which are characterized most of the time by a short apical V–O bond (≈1.6 Å) opposed to a very long apical V–O bond (≈2.4 Å), so that they can be described also as intermediate between pyramids and octahedra. Consequently the two kinds of coordinations may exist in the same framework, as shown for instance in several V(IV) phosphates such as $K_2V_2P_4O_{17}$ (*8*), $BaV_2P_2O_{10}$ (*9*), and $PbV_2P_2O_{10}$ (*10*) and in the mixed valent phosphate $Rb_6V_6P_6O_{31}$ (*11*). The greater ability of V(V) to adopt an octahedral coordination suggests the possibility of ordering of V(IV) and V(V) in agreement with the results obtained for $Rb_6V_6P_6O_{31}$ (*11*) in which V(V) is located in the octahedra, whereas V(IV) is in pyramidal coordination. In this respect the $BaV_2P_2O_{10}$ structure is of interest since in it V(IV) is located in two independent sites, octahedral and pyramidal respectively. The substitution of a univalent cation for barium should allow an ordering of V(V) and V(IV) between the two sorts of sites to be obtained. We report on the crystal structure of the mixed valent vanadium phosphate $AgV_2P_2O_{10}$, whose structure is very closely related to those of $BaV_2P_2O_{10}$ (*9*) and $PbV_2P_2O_{10}$ (*10*).

Experimental

Black single crystals of $AgV_2P_2O_{10}$ were isolated from a mixture of nominal composi-

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TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT

	Crystal data
Space group	$P2_1/C$
Cell dimensions	$a = 5.256(1)$ Å
	$b = 8.117(1)$ Å $\beta = 91.46(1)°$
	$c = 16.966(1)$ Å
Volume	$v = 723.6$ Å^3
z	4
d_{calc}	3.96
	Intensity measurement
λ (Mo $K\bar{\alpha}$)	0.71073 Å
Scan mode	$\omega - 2\theta$
Scan width (°)	$0.95 + 0.35 \tan \theta$
Slit aperture (mm)	$1.09 + \tan \theta$
Max θ (°)	45°
Standard reflections	three measured every 2000 sec (no decay)
Measured reflections	6375
Reflections with $I > 3\sigma$	2951
μ (mm^{-1})	5.59
Range h	$-10 + 10$
k	$0 + 16$
l	$0 + 33$
	Structure solution and refinement
Parameters refined	136
Agreement factors	$R = 0.028$, $R_W = 0.030$
δ/σ max	<0.004

TABLE II

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B(A2)
Ag	0.07526(5)	0.20627(3)	0.18857(2)	1.352(3)
V(1)	0.14413(8)	0.86962(6)	0.06988(3)	0.433(5)
V(2)	0.46419(9)	0.03216(6)	0.35275(3)	0.490(5)
P(1)	0.3664(1)	0.26446(8)	0.01677(4)	0.383(8)
P(2)	0.3564(1)	0.42347(8)	0.31759(4)	0.376(8)
O(1)	0.1727(4)	0.6911(3)	0.1095(1)	0.86(3)
O(2)	−0.1368(4)	0.8546(3)	−0.0134(1)	0.63(3)
O(3)	−0.1180(4)	0.9710(3)	0.1386(1)	0.73(3)
O(4)	0.3837(4)	0.8271(3)	−0.0141(1)	0.72(3)
O(5)	0.3988(4)	0.9799(3)	0.1413(1)	0.70(3)
O(6)	0.2285(4)	−0.0757(3)	0.3237(2)	1.14(3)
O(7)	0.3582(4)	0.2360(3)	0.3028(1)	0.78(3)
O(8)	0.6749(4)	0.0052(3)	0.2649(1)	0.75(3)
O(9)	0.6566(4)	−0.1367(3)	0.4057(1)	0.76(3)
O(10)	0.3416(4)	0.1103(3)	0.4478(1)	0.68(3)

Note. Anisotropically refined atoms are given in the isotropic equivalent displacement parameter, defined as $B = (4/3) [\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha]$.

tion $AgV_2P_2O_{10}$. The growing of these crystals was performed in two steps. First, a mixture of $AgNO_3$, $H(NH_4)_2PO_4$, and V_2O_5 with the molar ratio of 10 : 20 : 9 was heated to 653 K in order to eliminate CO_2, NH_3, and H_2O. In a second step the resulting finely ground product was mixed with an appropriate amount of vanadium (molar ratio of 2 with respect to the previous ones) and sealed in an evacuated silica ampoule. This sample was heated to 1173 K for 1 day, cooled to 973 K with a rate of 1 K per hr, and then quenched to room temperature. This method allowed blue and black crystals to be isolated from a sintered powder. All further attempts to obtain a pure phase have failed; a mixture was always obtained.

A black crystal of 0.129 × 0.116 × 0.09 mm along **a**, **b**, **c**, respectively was selected for the structure determination. The data were collected on an Enraf–Nonius CAD 4 diffractometer under the conditions reported on Table I. The reflections were corrected for the Lorentz, polarization, absorption, and secondary extinction effects. The structure was solved by the heavy atom method. The atomic coordinates and the anisotropic thermal factors were refined by a full matrix least squares method which led to $R = 0.028$ and $R_w = 0.030$ and to the coordinates of Table II.

Description of the Structure and Discussion

The structure of this mixed valent vanadium phosphate is closely related to that of the tetravalent vanadium phosphate $BaV_2P_2O_{10}$ (9). Its monoclinic cell derives from that of $BaV_2P_2O_{10}$ (Table III) by a contraction of the b parameter of about 1 Å, and an expansion of the c parameter of about 0.6 Å. The projection of the structure of these compounds along **a** (Fig. 1) allows

TABLE III

	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
$AgV_2P_2O_{10}$	5.256(1)	8.117(1)	16.966(1)	91.46(1)	723.6(2)
$PbV_2P_2O_{10}$	5.230(1)	8.581(1)	16.700(1)	91.01(1)	753.4(2)
$BaV_2P_2O_{10}$	5.220(1)	9.170(1)	16.325(1)	92.76(1)	780.6(2)

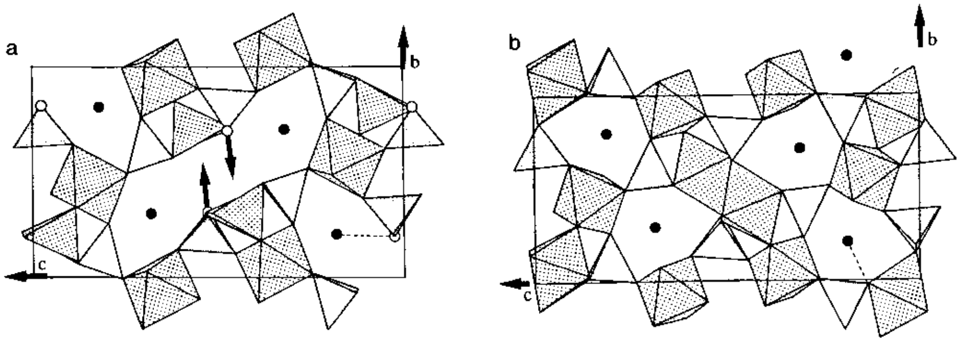

FIG. 1. (a) Projection along **a** of the $BaV_2P_2O_{10}$ structure: ● is the Ba atoms; ○ is the oxygen atom O(2). The arrows show the displacement of the O(2) atom pulling the polyhedra of the framework when Ba is replaced by Pb or Ag. (b) Projection along **a** of the $AgV_2P_2O_{10}$ structure. The dotted lines on the two structures show their respective A–O minimum bond lengths.

both their great similarity and their difference to be understood.

In $BaV_2P_2O_{10}$ (Fig. 1a) the $[V_2P_2O_{10}]_\infty$ host lattice is built up from VO_5 pyramids and VO_6 distorted octahedra forming an elongated tunnel running along **a**. In this structure the V(1) pyramid shares the four corners of its basal plane with PO_4 tetrahedra, whereas the fifth corner is linked to the V(2) octahedron; the V(2) octahedron shares five of its apices with four PO_4 tetrahedra and one VO_5 pyramid, the sixth corner being free. As a result the structure of $BaV_2P_2O_{10}$ can be described as $[VP_2O_9]_\infty$ columns of corner-sharing VO_5 pyramids and PO_4 tetrahedra running along **a** (Fig. 2a) and linked to each other through VO_6 octahedra.

In $AgV_2P_2O_{10}$ (Fig. 1b), one observes two kinds of distorted VO_6 octahedra, labeled V(1) and V(2), forming with the PO_4 tetrahedra six-sided tunnels running along **a**. In fact this structure derives from that $BaV_2P_2O_{10}$ by a distortion of the $[V_2P_2O_{10}]_\infty$ framework in such a way that the V(1) pyramid is replaced by a V(1) octahedron. Indeed the O(2) oxygen atoms belonging to the basal planes of two facing V(1) pyramids in $BaV_2P_2O_{10}$ are brought closer to each other (see arrows in Fig. 1a), so that the coordination of V(1) atoms can be described as a distorted octahedron or as a disymmetric square bipyramid. Consequently, the elongated tunnels of $BaV_2P_2O_{10}$ are split into two smaller six-sided tunnels for $AgV_2P_2O_{10}$ units built up from two edge-sharing V(1) octahedra. Thus the structure of $AgV_2P_2O_{10}$ can also be described as built up from $[V_4O_{20}]$ strings of edge and corner-sharing VO_6 octahedra linked through monophosphate groups (Fig. 2b).

The geometry of the PO_4 tetrahedra and V(2) octahedra is very similar to that observed in $BaV_2P_2O_{10}$ and $PbV_2P_2O_{10}$, as shown by the interatomic distances (Table IV). Note that the four equatorial V(2)–O bonds (1.86 to 1.93 Å) are shorter than those of the Ba and Pb compounds (1.94 to 2.03 Å), whereas the apical V(2)–O distances of 1.59 and 2.37 Å, respectively, are almost equal to those for Ba (1.61 and 2.38 Å) and Pb (1.60 and 2.37 Å. This fact is consistant with the valence 5 of V(2) in the Ag compound instead of 4 in the Ba and Pb ones.

The comparison of the V(1) pyramids of the barium and lead phosphates with the V(1) octahedra of the silver phosphate shows the spectacular but continuous transition from pyramidal to octahedral coordination. Indeed in the three structures the four equatorial V(1)–O distances are very similar, ranging from 1.96 to 2.02 Å for Ag (Table IV), and from 1.94 to 2.01 Å for Pb and Ba. In the same way, one of the apical V(1)–O bonds, the short one corresponding

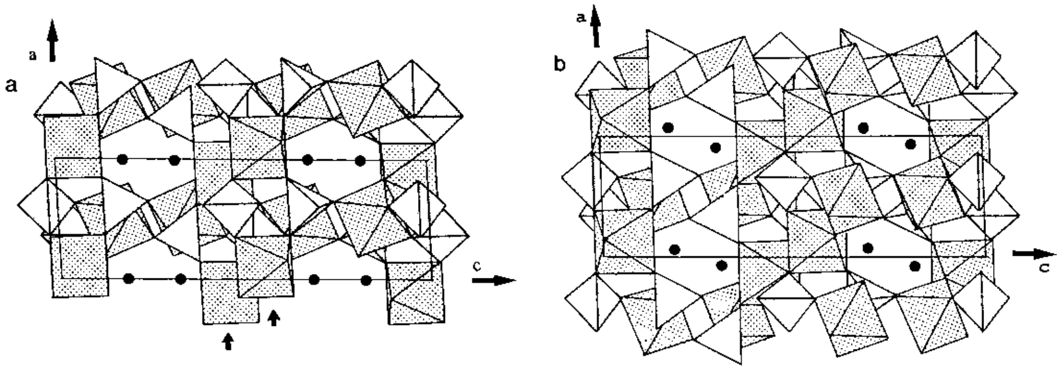

FIG. 2. (a) Projection along **b** of the $BaV_2P_2O_{10}$ structure. The arrows show the $[VP_2O_9]_\infty$ columns of corner-sharing VO_5 and $PO_4 \cdot [V_4O_{20}]_\infty$ units. (b) Projection along **b** of the $AgV_2P_2O_{10}$ structure showing the stacking of the $[V_4O_{20}]$ units.

to the vanadyl ion, does not vary significantly, ranging from 1.60 Å for Ag to 1.60 and 1.61 Å for Ba and Pb. The second apical V(1)–O(2) distance reveals the large displacement of the O(2) oxygen atom in the three structures. One indeed observes a V(1)–O(2) distance of 2.435 Å for the Ag-phase, which can be considered as a V–O bond, whereas it increases to 2.889 Å for the Pb phosphate and reaches 3.478 Å in the Ba compound, so that in the two latter phases the O(2) and V(1) atom belonging to two different basal planes cannot be considered as bounded any more. This structural evolution also shows that lead exhibits behavior intermediate between that of barium and silver.

The examination of the Ag–O distances (Table IV) shows that Ag^+ exhibits an eightfold coordination with five rather short distances ranging from 2.31 to 2.64 Å. The latter are significantly shorter than those observed for lead (2.49 to 2.69 Å) and especially for barium (2.70 to 2.75 Å), in agreement with the size of these three cations. Note that the unit cell volume of these compounds increases linearly as the shortest A–O distance of the AO polyhedron (A = Ag, Pb, Ba) increases (Fig. 3). It seems to us most probable that the size of the A cation in the tunnels influences drastically the coordination of V(1). It is indeed easy to understand that the O(2) atoms will be more and more strongly attracted as the size of the A cation decreases, changing progressively the coordination of V(1) from a VO_5 pyramid to a VO_6 octahedron. Attempts at synthesis of phosphates with smaller cations such as calcium or sodium are in progress in order to check this viewpoint.

The existence of a mixed valence for vanadium, according to the formula $AgV^{IV}V^{V}P_2O_{10}$, may also be the origin of the structural difference of this phase with respect to $BaV_2P_2O_{10}$ and $PbV_2P_2O_{10}$. Owing to the presence of two independent sites, it suggests a possible ordering of V(IV) and

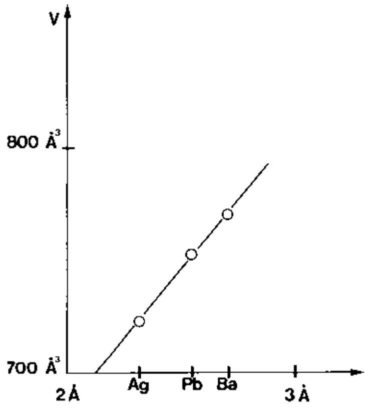

FIG. 3. Plot of the unit cell volume versus the A–O minimum bond lengths (A = Ba, Pb, Ag).

TABLE IV

V(1)	O(1)	O(2)	O(2^{x})	O(3)	O(4)	O(5)
O(1)	1.603(2)	2.930(3)	4.034(3)	2.789(3)	2.639(3)	2.677(3)
O(2)	107.3(1)	2.022(2)	2.795(3)	2.746(3)	2.745(3)	3.933(3)
O(2^{x})	175.2(1)	77.1(1)	2.435(2)	2.907(3)	2.934(3)	2.872(3)
O(3)	100.7(1)	86.0(1)	81.2(1)	2.004(2)	3.922(3)	2.716(3)
O(4)	95.2(1)	87.3(1)	83.1(1)	163.9(1)	1.956(2)	2.913(3)
O(5)	95.56(1)	156.7(1)	80.2(1)	85.6(1)	95.0(1)	1.994(2)

V(2)	O(1^{i})	O(6)	O(7)	O(8)	O(9)	O(10)
O(1^{i})	2.378(2)	3.962(3)	2.870(3)	2.715(3)	2.822(3)	2.832(3)
O(6)	177.3(1)	1.585(2)	2.646(3)	2.655(3)	2.661(3)	2.646(3)
O(7)	82.8(1)	97.0(1)	1.934(2)	2.597(3)	3.810(3)	2.667(3)
O(8)	78.1(1)	99.2(1)	85.5(1)	1.891(2)	2.655(3)	3.701(3)
O(9)	81.4(1)	98.6(1)	164.0(1)	88.5(1)	1.913(2)	2.708(3)
O(10)	82.8(1)	99.9(1)	89.2(1)	160.6(1)	91.6(1)	1.864(2)

P(1)	O(2^{ii})	O(4^{iii})	O(9^{iv})	O(10^{v})
O(2^{ii})	1.546(2)	2.530(3)	2.473(3)	2.528(3)
O(4^{iii})	111.7(1)	1.511(2)	2.529(3)	2.522(3)
O(9^{iv})	106.1(1)	111.5(1)	1.549(2)	2.494(3)
O(10^{v})	109.3(1)	110.9(1)	107.1(1)	1.552(2)

P(2)	O(3^{vi})	O(5^{i})	O(7)	O(8^{iv})
O(3^{vi})	1.523(2)	2.542(3)	2.507(3)	2.445(3)
O(5^{i})	113.4(1)	1.519(2)	2.528(3)	2.529(3)
O(7)	109.7(1)	111.3(1)	1.542(2)	2.473(3)
O(8^{iv})	105.2(1)	110.8(1)	106.0(1)	1.555(2)

Ag–O(2^{ii})	3.038(2) Å
Ag–O(3^{viii})	2.314(2) Å
Ag–O(5^{viii})	2.642(2) Å
Ag–O(6^{ix})	2.389(2) Å
Ag–O(7)	2.425(2) Å
Ag–O(8^{vii})	2.985(2) Å
Ag–O(9^{iv})	2.506(2) Å
Ag–O(8^{iv})	2.860(2) Å

Symmetry code

i	$1 - x$	$y - \frac{1}{2}$	$\frac{1}{2} - z$
ii	$-x$	$1 - y$	$-z$
iii	$1 - x$	$1 - y$	$-z$
iv	$1 - x$	$\frac{1}{2} + y$	$\frac{1}{2} - z$
v	x	$\frac{1}{2} - y$	$z - \frac{1}{2}$
vi	$-x$	$y - \frac{1}{2}$	$\frac{1}{2} - z$
vii	$x - 1$	y	z
viii	x	$y - 1$	z
ix	$-x$	$\frac{1}{2} + y$	$\frac{1}{2} - z$
x	$-x$	$2 - y$	$-z$

V(V). The sum of the electrostatic valences determined from the Brown and Altermatt curves (*12*) supports this hypothesis. One indeed obtains the calculated valences of 4.06, 5.09, and 1.14 for V(1), V(2), and Ag, respectively. Thus the tetravalent vanadium appears to be located in the V(1) octahedral sites, minimizing the V–V coulombic repulsion between two edge-sharing octahedra of the V_2O_{10} units, whereas V(V) sits in the V(2) octahedral sites, which are only corner-shared with the PO_4 tetrahedra and the V(1) octahedra.

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