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# Crystal structure of the mixed-metal thiophosphate $Nb_{1.18}V_{0.82}PS_{10}$

Joobin Sun, Jiyun Heo and Hoseop Yun*

Department of Energy Systems Research and Department of Chemistry, Ajou University, Suwon 443-749, Republic of Korea. *Correspondence e-mail: hsyun@ajou.ac.kr
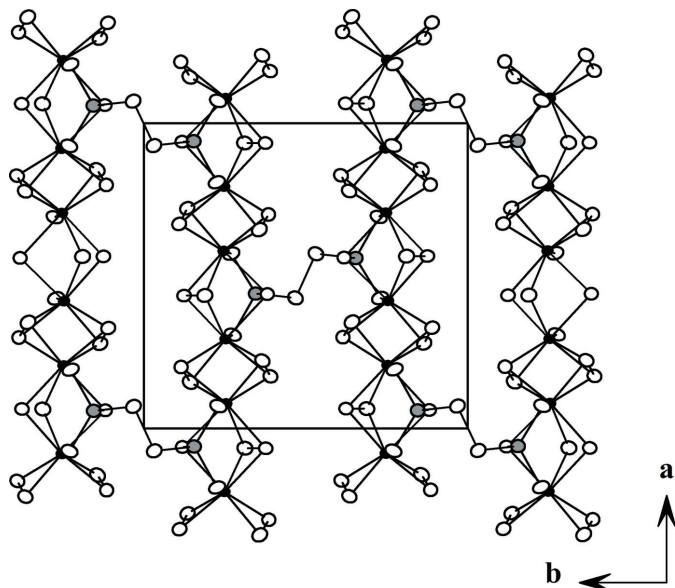
The mixed-metal thiophosphate, $Nb_{1.18}V_{0.82}PS_{10}$ (niobium vanadium phosphorus decasulfide), has been prepared though solid state reactions using an alkali-metal halide flux. The title compound is isostructural with two-dimensional Nb_2PS_{10}. $[M_2S_{12}]$ (M = Nb or V) dimers built up from two bicapped trigonal prisms and tetrahedral $[PS_4]$ units share sulfur atoms to construct $^1_\infty[M_2PS_{10}]$ chains along the a axis. These chains are linked through the disulfide bonds between $[PS_4]$ units in adjacent chains to form layers parallel to the ab plane. These layers then stack on top of each other to complete the three-dimensional structure with van der Waals gaps. The M sites are occupied by 59% of Nb and 41% of V and the average $M-S$ and $M-M$ distances in the title compound are in between those of V_2PS_{10} and Nb_2PS_{10}. The classical charge balance of the title compound can be represented by $[(Nb/V)^{4+}]_2[P^{5+}][S^{2-}]_3[S^-]_7$.

1. Chemical context

Ternary group 5 metal thiophosphates, M_2PS_{10} (M = V, Nb) have been reported to have low-dimensional structures with partially filled d orbitals which can accommodate electrons. Therefore, they are of potential importance as cathode materials for high-energy density lithium batteries (Rouxel, 1986). While both are composed of the same linear chains, *i.e.* $^1_\infty[M_2PS_{10}]$, V_2PS_{10} has a chain structure (Brec *et al.*, 1983a) and Nb_2PS_{10} adopts a layered structure (Brec *et al.*, 1983b). To understand the cause of different dimensionality between these phases, we have conducted research on the synthesis of the mixed phases, $(Nb/V)_2PS_{10}$. We report here
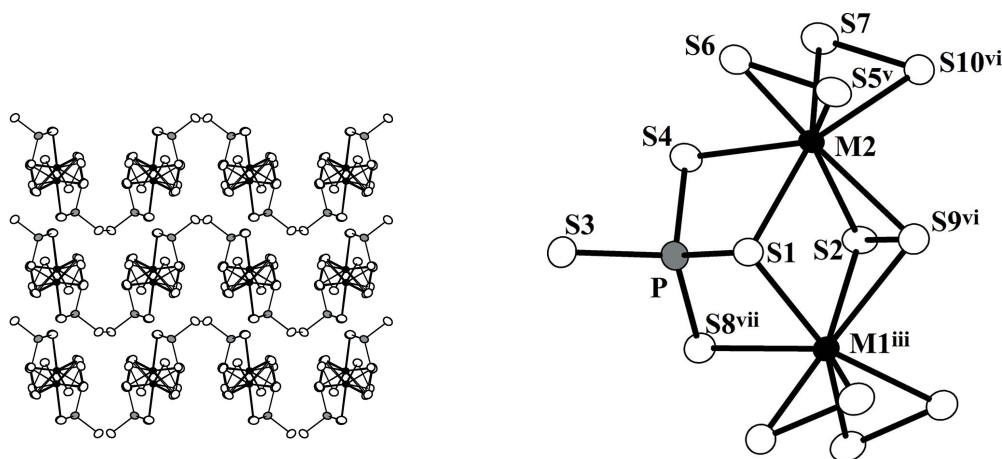
Figure 1
A view of the $[M_2S_{12}]$ dimer unit (M = Nb or V) and its neighbouring tetrahedral $[PS_4]$ group. Open circles are S atoms, filled circle are M atoms and gray circles are P atoms. Displacement ellipsoids are drawn at the 60% probability level.
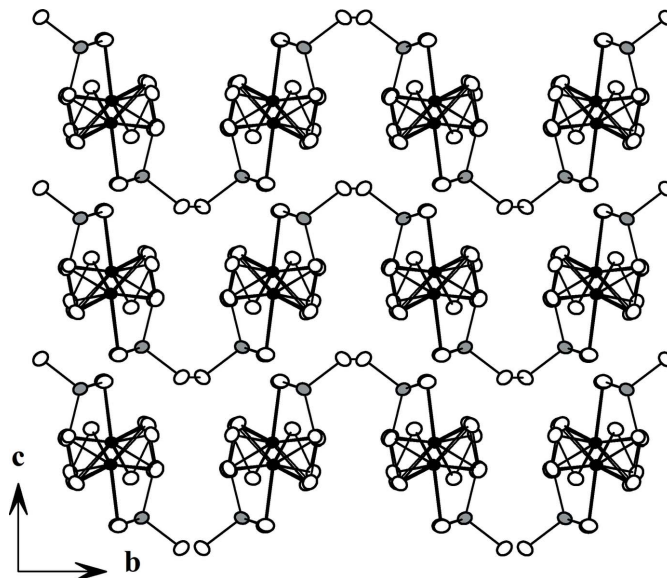
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Figure 2
View of the M_2PS_{10} layers showing the two-dimensional nature of the compound. Atoms are as marked in Fig. 1.

Figure 3
The structure of $Nb_{1.18}V_{0.82}PS_{10}$, viewed down the c axis.

the synthesis and structural characterization of a mixed-metallic thiophosphate, namely $Nb_{1.18}V_{0.82}PS_{10}$.

2. Structural commentary

The title compound, Nb-rich $Nb_{1.18}V_{0.82}PS_{10}$, is isostructural with Nb_2PS_{10} and detailed descriptions of this structural type have been given previously (Brec *et al.*, 1983*b*). The usual $[M_2S_{12}]$ (M = Nb, V) dimeric units (Yun *et al.*, 2003) built up from two bicapped trigonal prisms and tetrahedral $[PS_4]$ units (Yu & Yun, 2011) share S atoms (Fig. 1) to construct an $^1_\infty[M_2PS_{10}]$ chain along the a axis. These chains are linked through the disulfide bonds between $[PS_4]$ units in adjacent chains to form layers parallel to the ab plane (Fig. 2). These layers then stack on top of each other to complete the three-dimensional structure with van der Waals gaps shown in Fig. 3. There is no bonding interaction, only van der Waals forces, between the layers.

The M sites occupied by statistically disordered Nb (59%) and V (41%) are surrounded by eight S atoms in a bicapped trigonal prismatic fashion and the average M—S bond length [2.51 (6) Å] in the title compound is between those of Nb_2PS_{10} [2.54 (6) Å; Brec *et al.*, 1983*b*] and V_2PS_{10} [2.46 (7) Å; Brec *et al.*, 1983*a*]. The M atoms associate in pairs, with $M\cdots M$ interactions alternating in the sequence of one short [2.855 (1) Å] and one long distance [3.728 (1) Å]. This M—M distance, which is longer than that of V_2PS_{10} [2.852 (2) Å] and shorter than that of Nb_2PS_{10} [2.869 (1) Å], is indicative of a d^1–d^1 interaction. The long distance implies that there is no significant bonding (Angenault *et al.*, 2000), which is consistent with the highly resistive nature of the crystal since no inter-metallic bond can be set. The P—S distances in the tetrahedral $[PS_4]$ unit are in good agreement with those found in other thiophosphates (Brec *et al.*, 1983*b*). There is no terminal S

atom in this unit and this is responsible for the absence of the rather short P—S distances (< 2.0 Å) found in V_2PS_{10} (Brec *et al.*, 1983*a*) and other related compounds, such as KNb_2PS_{10} (Do & Yun, 1996).

The classical charge balance of the title compound can be represented by $[(Nb/V)^{4+}]_2[P^{5+}][S^{2-}]_3[S^-]_7$. This study does not provide conclusive results on the different dimensionality between Nb_2PS_{10} and V_2PS_{10} and thus we believe that further studies to search for V-rich phases are necessary.

3. Synthesis and crystallization

The compound $Nb_{1.18}V_{0.82}PS_{10}$ was prepared by the reaction of the elements Nb, V, P and S by the use of the reactive alkali metal halides. A combination of the pure elements, Nb powder (CERAC 99.8%), V powder (CERAC 99.5%), P powder (CERAC 99.95%) and S powder (Aldrich 99.999%) were mixed in a fused-silica tube in an Nb:V:P:S molar ratio of 1:1:1:10 with KCl. The mass ratio of the reactants and the halides flux was 2:1. The tube was evacuated to 0.133 Pa, sealed and heated gradually (100 K h^{-1}) to 650 K, where it was kept for 12 h. The tube was cooled to 473 K at a rate of 4 K h^{-1} and then quenched to room temperature. The excess halides were removed with distilled water and black needle shaped crystals were obtained. The crystals are stable in air and water. A qualitative X-ray fluorescence analysis of selected crystals indicated the presence of Nb, V, S and P. The final composition of the title compound was determined by single-crystal X-ray diffraction.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The refinement of the model with occupational disorder on the M sites caused significant

Table 1
Experimental details.

Crystal data	
Chemical formula	$Nb_{1.18}V_{0.82}PS_{10}$
M_r	502.97
Crystal system, space group	Orthorhombic, $P2_12_12$
Temperature (K)	290
a, b, c (Å)	12.8472 (4), 13.6212 (4), 7.1972 (3)
V (Å³)	1259.47 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	3.42
Crystal size (mm)	$0.20 \times 0.02 \times 0.02$
Data collection	
Diffractometer	Rigaku R-AXIS RAPID S
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.503, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11897, 2757, 2053
R_{int}	0.081
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.103, 1.13
No. of reflections	2757
No. of parameters	121
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	1.04, −1.06
Absolute structure	Flack (1983)
Absolute structure parameter	0.64 (13)

Computer programs: *RAPID-AUTO* (Rigaku, 2006), *SHELXS2013* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *WinGX* (Farrugia, 2012).

decrease of the *R* factor ($wR2 = 0.103$) in comparison with the case where full occupation by either metal had been considered ($wR2 > 0.176$). No evidence was found for ordering of this site and thus a statistically disordered structure is assumed. Also the displacement parameters in the disordered model became plausible. The disordered atoms were supposed to have the same displacement parameters. The Nb:V ratios on both *M* sites are almost the same, *i.e.* 59:41. The program *STRUCTURE TIDY* (Gelato & Parthé, 1987) was used to standardize the positional parameters. A difference Fourier synthesis calculated with phase based on the final parameters shows that the highest residual electron density (1.04 e Å⁻³) is 1.40 Å from the *M*1 site and the deepest hole (−1.06 e Å⁻³) is 0.79 Å from the *M*2 site.

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Computing details

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO* (Rigaku, 2006); data reduction: *RAPID-AUTO* (Rigaku, 2006); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Niobium vanadium phosphorus decasulfide

Crystal data

Nb$_{1.18}$V$_{0.82}$PS$_{10}$	$F(000) = 969$
$M_r = 502.97$	$D_x = 2.653$ Mg m^{-3}
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2 2ab	Cell parameters from 8753 reflections
$a = 12.8472$ (4) Å	$\theta = 3.2–27.5°$
$b = 13.6212$ (4) Å	$\mu = 3.42$ mm^{-1}
$c = 7.1972$ (3) Å	$T = 290$ K
$V = 1259.47$ (8) Å^3	Needle, black
$Z = 4$	$0.2 \times 0.02 \times 0.02$ mm

Data collection

Rigaku R-AXIS RAPID S diffractometer	11897 measured reflections
Radiation source: Sealed X-ray tube	2757 independent reflections
Graphite monochromator	2053 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.081$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$\theta_{max} = 27.0°, \theta_{min} = 3.2°$
	$h = -16\rightarrow14$
	$k = -17\rightarrow17$
$T_{min} = 0.503, T_{max} = 1.000$	$l = -9\rightarrow9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 1.1529P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.103$	
$S = 1.13$	$(\Delta/\sigma)_{max} < 0.001$
2757 reflections	$\Delta\rho_{max} = 1.04$ e Å^{-3}
121 parameters	$\Delta\rho_{min} = -1.06$ e Å^{-3}
0 restraints	Absolute structure: Flack (1983)
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.64 (13)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Nb1	0.08230 (7)	0.74603 (8)	0.06349 (16)	0.0193 (3)	0.5889
V1	0.08230 (7)	0.74603 (8)	0.06349 (16)	0.0193 (3)	0.4111
Nb2	0.20780 (7)	0.24841 (8)	0.06671 (16)	0.0183 (3)	0.5856
V2	0.20780 (7)	0.24841 (8)	0.06671 (16)	0.0183 (3)	0.4144
S1	0.0601 (2)	0.11893 (17)	0.1005 (4)	0.0233 (6)	
S2	0.0647 (2)	0.37577 (18)	0.1107 (4)	0.0258 (6)	
S3	0.0727 (2)	0.03201 (19)	0.5538 (4)	0.0285 (6)	
S4	0.1930 (2)	0.22558 (19)	0.4241 (4)	0.0284 (6)	
S5	0.2221 (2)	0.6344 (2)	0.1672 (4)	0.0277 (7)	
S6	0.3292 (2)	0.10963 (19)	0.0949 (4)	0.0284 (7)	
S7	0.3483 (2)	0.3569 (2)	0.1743 (4)	0.0292 (7)	
S8	0.4267 (2)	0.27029 (19)	0.5806 (4)	0.0284 (6)	
S9	0.5644 (2)	0.18846 (18)	0.1448 (4)	0.0275 (6)	
S10	0.7986 (2)	0.11500 (19)	0.0879 (5)	0.0275 (7)	
P	0.0585 (2)	0.15464 (19)	0.3772 (3)	0.0236 (6)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nb1	0.0164 (5)	0.0218 (5)	0.0197 (6)	0.0011 (5)	0.0007 (4)	−0.0009 (6)
V1	0.0164 (5)	0.0218 (5)	0.0197 (6)	0.0011 (5)	0.0007 (4)	−0.0009 (6)
Nb2	0.0145 (5)	0.0214 (5)	0.0192 (6)	−0.0012 (5)	0.0009 (4)	0.0013 (6)
V2	0.0145 (5)	0.0214 (5)	0.0192 (6)	−0.0012 (5)	0.0009 (4)	0.0013 (6)
S1	0.0206 (12)	0.0257 (12)	0.0238 (14)	0.0001 (14)	0.0004 (14)	0.0006 (10)
S2	0.0200 (12)	0.0271 (13)	0.0303 (15)	0.0006 (14)	0.0024 (14)	−0.0042 (10)
S3	0.0256 (13)	0.0319 (13)	0.0281 (14)	−0.0039 (13)	−0.0051 (13)	0.0078 (12)
S4	0.0221 (12)	0.0388 (16)	0.0242 (14)	−0.0074 (13)	−0.0013 (13)	0.0023 (13)
S5	0.0234 (14)	0.0301 (15)	0.0296 (17)	0.0041 (13)	0.0029 (12)	0.0047 (13)
S6	0.0231 (14)	0.0288 (14)	0.0333 (19)	−0.0023 (14)	0.0017 (13)	0.0054 (13)
S7	0.0267 (15)	0.0326 (15)	0.0283 (17)	−0.0050 (14)	0.0009 (12)	−0.0067 (14)
S8	0.0233 (13)	0.0386 (15)	0.0233 (14)	−0.0064 (13)	−0.0030 (13)	0.0026 (12)
S9	0.0248 (13)	0.0334 (14)	0.0243 (14)	−0.0014 (14)	−0.0004 (13)	0.0023 (11)
S10	0.0236 (14)	0.0258 (14)	0.0332 (18)	−0.0002 (13)	−0.0011 (14)	0.0069 (13)
P	0.0223 (13)	0.0283 (13)	0.0202 (14)	0.0001 (15)	0.0013 (12)	0.0036 (10)

Geometric parameters (Å, º)

Nb1—S10[i]	2.440 (3)	Nb2—S5[v]	2.461 (3)
Nb1—S7[ii]	2.450 (3)	Nb2—S10[vi]	2.462 (3)
Nb1—S6[ii]	2.458 (3)	Nb2—S9[vi]	2.540 (3)
Nb1—S5	2.469 (3)	Nb2—S2	2.547 (3)
Nb1—S9[ii]	2.533 (3)	Nb2—S4	2.598 (3)
Nb1—S2[iii]	2.537 (3)	Nb2—S1	2.602 (3)
Nb1—S8[iv]	2.585 (3)	P—S1	2.050 (3)
Nb1—S1[iii]	2.608 (3)	P—S3	2.107 (3)
Nb1—Nb2[ii]	2.8549 (13)	P—S4	2.008 (4)
Nb2—S7	2.458 (3)	P—S8[vii]	2.002 (4)
Nb2—S6	2.459 (3)		
S8[vii]—P—S4	117.17 (16)	S8[vii]—P—S3	112.75 (17)
S8[vii]—P—S1	106.08 (17)	S4—P—S3	101.85 (16)
S4—P—S1	105.61 (17)	S1—P—S3	113.40 (15)

Symmetry codes: (i) −x+1, −y+1, z; (ii) −x+1/2, y+1/2, −z; (iii) −x, −y+1, z; (iv) −x+1/2, y+1/2, −z+1; (v) −x+1/2, y−1/2, −z; (vi) x−1/2, −y+1/2, −z; (vii) x−1/2, −y+1/2, −z+1.