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Synthesis, Characterization, and Crystal Structure of a New Truly One-Dimensional Compound: PV_2S_{10}

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PV_2S_{10} was obtained by heating the elements in stoichiometric proportions at 490°C in evacuated Pyrex tubes. The crystal symmetry is monoclinic, space group $P2_1/c$, with the unit cell parameters a = 12.734(8) Å, b = 7.349(7) Å, c = 23.662(4) Å, β = 95°22(1), V = 2205(4) Å^3, and Z = 8. The structure was solved from 2269 independant reflexions, and anisotropic least squares refinement gave R = 0.036 with 236 variables. The structure can be described as made of $[V_2S_{12}]$ units forming endless chains themselves linked, two by two, by $[PS_4]$ tetrahedra. In these units each vanadium is surrounded by eight sulfur atoms (mean d_{V-S} = 2.459 Å) arranged in a distorted bicapped triangular prism. Two of these prisms shared a rectangular face to form $[V_2S_{12}]$ groups, in which intercationic distances implied vanadium–vanadium bonds (mean d_{V-V} = 2.852(2) Å). Between the infinite double chains, only S–S weak van der Waals' bonds exist. More than two thirds of the sulfur atoms are present as $[S–S]^{-II}$ pairs, (mean d_{S-S} = 2.015 Å); the rest are S^{-II} anions.

1. Introduction

It has been recently shown (*1*, *2*) that phosphorus can be used as an intercalated cation to stabilize layered structures such as VS_2 or $CrSe_2$. In the former case, the formation of a phase with the composition $P_{0.2}VS_2$ has been found, the phosphorus atoms being present as $[P_2]$ pairs in the van der Waals' gap octahedral sites of the CdI_2 like structure of VS_2 (*3*).

Stabilization of other binary chalcogenides of transition elements must be possible and, in the course of such a research in the P–V–S system, the occurrence of one-dimensional PV_2S_{10} was observed. We report in this article the synthesis, characterization, and crystal structure of this new compound.

2. Experimental

PV_2S_{10} is obtained by heating the high purity elements in sealed tubes at 490°C for 10 days followed by a 1 day cooling. This synthesis yields fiber-like black crystals which analysis by means of a microprobe (microsonde ouest CNEXO) leads to P : 7.0% (calc. 6.8), V : 22.3% (calc. 22.5), and S : 70.1% (calc. 70.7). Single crystal X-ray analysis shows PV_2S_{10} to be monoclinic, space group $P2_1/c$. The cell parameters a = 12.734(8) Å, b = 7.349(7) Å, c = 23.662(4) Å, β = 95°22(1) were least squares refined from Guinier powder spectra (Guinier Nonius FR 552, $\lambda(CuK\alpha1)$ = 1.54051 Å, Si as standard) (Table I) and from 25 reflexions collected on an ENRAF–NONIUS CAD 4 diffractometer using monochromatized

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TABLE I

PV_2S_{10} INDEXED GUINIER POWDER SPECTRUM

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	hkl	I/I_0[a]	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	hkl	I/I_0[a]
7.025	7.016	011	70	2.584	2.585	$40\bar{6}$	60
6.379	6.359	110	30	2.529	2.528	$22\bar{6}$	5
5.893	5.891	004	100	2.455	2.455	$32\bar{5}$	20
5.711	5.706	$11\bar{2}$	5	2.437	2.437	031	5
5.360	5.367	013	90	2.407	2.405	130	30
4.774	4.769	$21\bar{1}$	50	2.388	2.390 2.390	$51\bar{2}$ $31\bar{8}$	50
4.427	4.423	$11\bar{4}$	10	2.364	2.364	406	30
4.233	4.226 4.228	114 $21\bar{3}$	30	2.351	2.349	132	5
3.971	3.967	015	10	2.331	2.330	325	10
3.679	3.675	020	40	2.299	2.299 2.298	$41\bar{7}$ 028	40
3.497	3.485	$21\bar{5}$	5	2.262	2.262	034	10
3.418	3.412	$11\bar{6}$	10	2.241	2.240	$13\bar{4}$	5
3.253	3.250	$12\bar{3}$	5	2.212	2.214	134	30
3.229	3.228	$31\bar{4}$	10	2.172	2.174	035	5
3.115	3.118	024	20	2.114	2.114 2.114	$42\bar{6}$ 600	50
3.061	3.060	017	50	2.101	2.103	$33\bar{2}$	5
3.007	3.007	314	20	2.066	2.067 2.066	$13\bar{6}$ 408	30
2.919	2.919	$41\bar{1}$	20	2.057	2.057 2.057	$31\overline{10}$ 0111	20
2.861	2.860	$12\bar{5}$	30	2.032	2.033	$41\bar{9}$	30
2.793	2.791	$31\bar{6}$	40	2.009	2.010	$61\bar{3}$	5
2.772	2.769	$20\bar{8}$	5	1.988	1.988	426	5
2.691	2.691	404	40	1.979	1.979	$40\overline{10}$	40
2.658	2.658	413	5	1.963	1.963 1.964	$32\bar{9}$ 0012	20

[a] Estimated intensities.

MoKα radiation. Both results were identical within errors. A long needle-like crystal (several millimeters long) was used for intensity data collection. Because of the true one-dimensional character of PV_2S_{10} (see structure study below), cutting of the acicular crystals to reasonable length proved impossible without splitting them in many smaller ones. For that reason, and also due to the low linear absorption coefficient (μ = 74 cm^{-1}) and small width of the sample (Fig. 1), no absorption corrections were made. After Lorentz and polarization factors corrections and averaging, 2269 independant reflexions with intensities $I > 3\sigma(I)$ were used for the refinement of the structure, the measured range being 3–35° with the ω scan method. Density measurements made according to the buoyancy principle lead to $d_{exp} = 2.75$ in good agreement with a calculated density ($d_{calc} = 2.77$) for eight molecular weights per cell. Magnetic susceptibility data were obtained on ground powder using a Faraday balance and a field strength of 5.0 kOe in a 4.2–300 K temperature range.

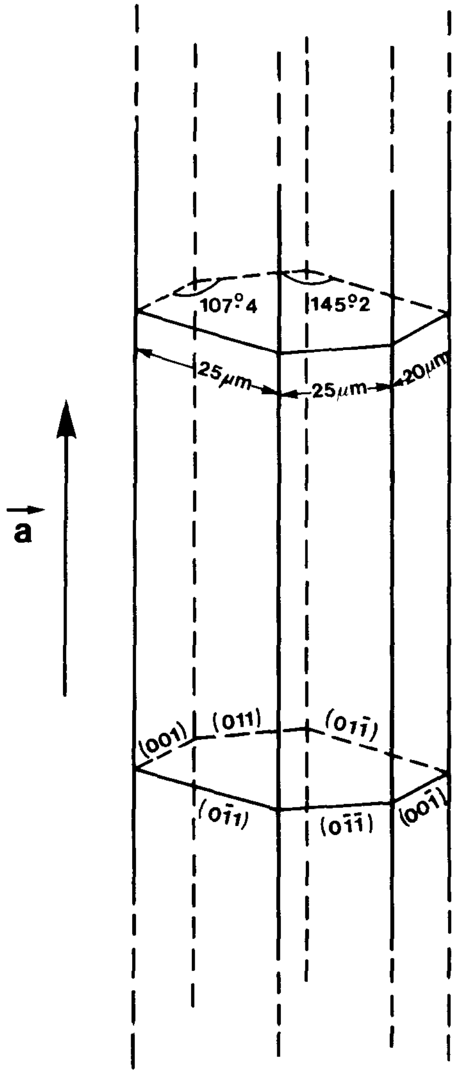

FIG. 1. PV_2S_{10} crystal size and planes.

3. Structure Determination

Because of the very close scattering factors of the atoms P, V, and S, the use of a Patterson map proved rather difficult. However, calculations with $(h0l)$ reflexions gave the x and z coordinates of the atoms. The whole set of data leads to y values and satisfactory reliability factors. Calculations without absorption correction and with isotropic temperature factors gave $R = 0.079$ and $wR = 0.088$.[1] At that point a Fourier difference map showed no significant electron density ($E_d < 0.7\ e/\text{Å}^3$). Refinement with anisotropic temperature factors leads to $R = 0.036$ and $wR = 0.042$, the extinction coefficient being equal to $0.302.10^{-7}$. Table II lists the final fractional coordinates of the 26 independant atoms of the cell. (A list of structure factors can be obtained from the authors upon request.)

4. Structural Results and Discussion

Figure 2 represents a projection of the structure along the b axis. Four infinite chains built of $[V_2S_{12}]$ units run along the a axis, the growth direction of the needles. These $[V_2S_{12}]$ groups are made of distorted bicapped trigonal prisms of sulfur, sharing a rectangular face, the vanadium atoms being present as pairs with a V–V bond going through this face (Fig. 3). One of the vanadiumlinked bicapping sulfur atoms (S(1)) of each prism lies above the center of a noncommon rectangular face and is linked to phosphorus, the other (S(24)) is displaced from the center of the second noncommon rectangular face and is bonded to the vanadium of the following prisms. Four $S_2^{-\text{II}}$ pairs are found in a given $[V_2S_{12}]$ unit; for example, in Fig. 3 (S(12)–S(14)), (S(11)–S(13)), (S(23)–S(24)), and (S(15)–S(16)), with the expected short interatomic distances (see Table III). As in $TaPS_6$ (*4*), and NbS_2Cl_2 (*5*) the $[S–S]^{-\text{II}}$ pair distances are significantly shorter than in VS_4 (*6*), FeS_2 (*7*), NbS_3 (*8*), and TaS_3 (*9*), for example, with an average of 2.015(2) Å. As can be seen in Fig. 3, some of the bicapping atoms (e.g., S(24)) of a given prism form a pair with one of the coordinating sulfurs (e.g., S(23)). One observes short distances between this bicapping species and the neigh-

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[1] $R = \Sigma||F_o| - |Fc||/\Sigma|Fo|$ $wR = [\Sigma w(|Fo| - |F_c|)^2/wF_o^2]^{\frac{1}{2}}$ with $w = 1$.

TABLE II

PV_2S_{10} POSITIONAL AND THERMAL PARÁMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS[a]

Atom	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	B_{eq}
V-1	0.3134(1)	0.5609(3)	0.86570(7)	0.00071(7)	0.0074(3)	0.00051(2)	0.0003(3)	0.00047(7)	0.0001(2)	1.05
V-2	0.5254(1)	0.4397(3)	0.86326(7)	0.00100(7)	0.0062(3)	0.00058(2)	0.0003(3)	0.00044(7)	−0.0001(2)	1.08
V-3	0.8133(1)	0.4457(3)	0.86298(7)	0.00106(7)	0.0059(3)	0.00056(2)	−0.0005(3)	0.00056(7)	−0.0003(2)	1.05
V-4	0.0259(1)	0.5672(3)	0.86634(7)	0.00086(6)	0.0065(3)	0.00056(2)	−0.0007(3)	0.00051(7)	−0.0003(2)	1.05
S-1	0.3075(2)	0.9122(4)	0.8740(1)	0.0018(1)	0.0078(5)	0.00157(5)	−0.0007(4)	0.0019(1)	−0.0002(3)	2.05
S-2	0.5370(2)	0.0903(4)	0.8574(1)	0.0013(1)	0.0085(5)	0.00111(5)	0.0002(4)	0.0002(1)	−0.0000(3)	1.72
S-3	0.8028(2)	0.0983(4)	0.8556(1)	0.0018(1)	0.0082(5)	0.00125(5)	0.0001(4)	0.0017(1)	−0.0006(3)	1.85
S-4	0.0403(2)	0.9178(4)	0.8758(1)	0.0012(1)	0.0075(5)	0.00132(5)	0.0013(4)	−0.0001(1)	0.0001(3)	1.79
S-11	0.3844(2)	0.3799(4)	0.7920(1)	0.0012(1)	0.0136(6)	0.00066(4)	0.0017(4)	0.0001(1)	−0.0017(3)	1.73
S-12	0.4044(2)	0.3571(4)	0.9316(1)	0.0017(1)	0.0104(5)	0.00069(4)	0.0010(4)	0.0006(1)	0.0014(2)	1.61
S-13	0.4289(2)	0.6407(4)	0.7964(1)	0.0015(1)	0.0124(5)	0.00073(4)	0.0026(4)	0.0010(1)	0.0020(3)	1.73
S-14	0.4575(2)	0.6165(4)	0.9363(1)	0.0017(1)	0.0104(5)	0.00072(4)	0.0018(4)	0.0002(1)	−0.0009(3)	1.65
S-15	0.6572(2)	0.4503(4)	0.7928(1)	0.0011(1)	0.0089(4)	0.00065(4)	−0.0001(4)	0.0005(1)	−0.0008(2)	1.35
S-16	0.6650(2)	0.6633(4)	0.8468(1)	0.0015(1)	0.0067(4)	0.00081(4)	0.0002(4)	0.0006(1)	0.0001(2)	1.39
S-17	0.6822(2)	0.3712(4)	0.9340(1)	0.0013(1)	0.0076(4)	0.00065(4)	0.0005(4)	0.0004(1)	0.0002(2)	1.30
S-18	0.6757(2)	0.9261(4)	0.9695(1)	0.0026(1)	0.0086(5)	0.00096(4)	−0.0027(5)	−0.0001(1)	0.0014(3)	1.90
S-19	0.8862(2)	0.6588(4)	0.7985(1)	0.0014(1)	0.0109(5)	0.00081(4)	−0.0016(4)	0.0003(1)	0.0011(3)	1.68
S-20	0.9057(2)	0.6167(4)	0.9373(1)	0.0016(1)	0.0091(5)	0.00069(4)	−0.0011(4)	0.0007(1)	−0.0011(2)	1.49
S-21	0.9204(2)	0.3982(4)	0.7907(1)	0.0018(1)	0.0120(5)	0.00075(4)	−0.0021(5)	0.0007(1)	−0.0018(3)	1.79
S-22	0.9560(2)	0.3587(4)	0.9312(1)	0.0016(1)	0.0092(5)	0.00068(4)	−0.0010(4)	0.0003(1)	0.0005(2)	1.51
S-23	0.1579(2)	0.5862(4)	0.7967(1)	0.0012(1)	0.0103(5)	0.00056(4)	0.0003(4)	0.0004(1)	0.0010(2)	1.41
S-24	0.1642(2)	0.3500(4)	0.8408(1)	0.0016(1)	0.0067(4)	0.00077(4)	0.0003(4)	0.0004(1)	−0.0003(2)	1.39
S-25	0.1828(2)	0.6078(4)	0.9392(1)	0.0010(1)	0.0077(4)	0.00062(4)	0.0001(4)	0.0006(1)	−0.0000(2)	1.21
S-26	0.1755(2)	0.0555(4)	0.9873(1)	0.0027(1)	0.0101(5)	0.00099(4)	0.0032(5)	0.0001(1)	−0.0022(3)	2.05
P-1	0.6789(2)	0.1147(4)	0.9017(1)	0.0012(1)	0.0064(4)	0.00087(4)	−0.0000(4)	0.0006(1)	0.0006(2)	1.35
P-2	0.1823(2)	0.8756(4)	0.9172(1)	0.0013(1)	0.0074(5)	0.00090(4)	−0.0005(4)	0.0008(1)	0.0008(3)	1.46

[a] The last column is the isotropic B equivalent (Å^2).

boring sulfur (S(25)) with a mean value of 2.984(2) Å, quite different from the mean value of 3.344 Å for the S–S distances between regular S^{-II} anions in this structure. Some degree of bonding corresponding to a tendency to $[S_3]$ group formation is suggested. Eight such units are present by unit cell. Within the chains, the V–V distances alternate between 2.852(2) Å and 3.672(3) Å, respectively, as observed in VS_4 (2.841 and 3.214 Å), implying cation–cation bonding. Vanadium atoms of neighboring chains are far apart with the shortest interchain distance of 5.780 Å. The mean V–S distance is equal to 2.459 Å.

To form a chain, the $[V_2S_{12}]$ units are linked together by the sulfur–sulfur edge of the trigonal prisms and by the sulfur atom located off one of the rectangular faces of the sulfur trigonal prism (see scheme Fig. 4). Hence the formulation of each line: $[V_2S_9]_\infty$.

Two successive chains corresponding to each other by the inversion center are linked by two $[P_2S_8]$ units (Fig. 2). Both constituent $[PS_4]$ tetrahedra are attached by $[S_2]^{-II}$ groups, the other sulfur atoms belonging to both adjacent $[V_2S_9]_\infty$ chains (Fig. 5).

Table IV gathers the main angles and distances in the tetrahedra. The average interatomic P–S distance is equal to 2.042 Å. The longer one corresponding to the sulfur atoms engaged in the $(S_2)^{-II}$ pairing, a fairly short P–S bond being calculated at 1.993(2) Å.

Between the double chains, and as can be seen clearly both from structure projection of Figs. 2 and 6, only weak bondings exist corresponding to van der Waal's forces between sulfur atoms otherwise engaged either in V–S or in P–S bonds. In that gap, the sulfur–sulfur distances span distances from 3.215 to 3.877 Å (see Table V). This

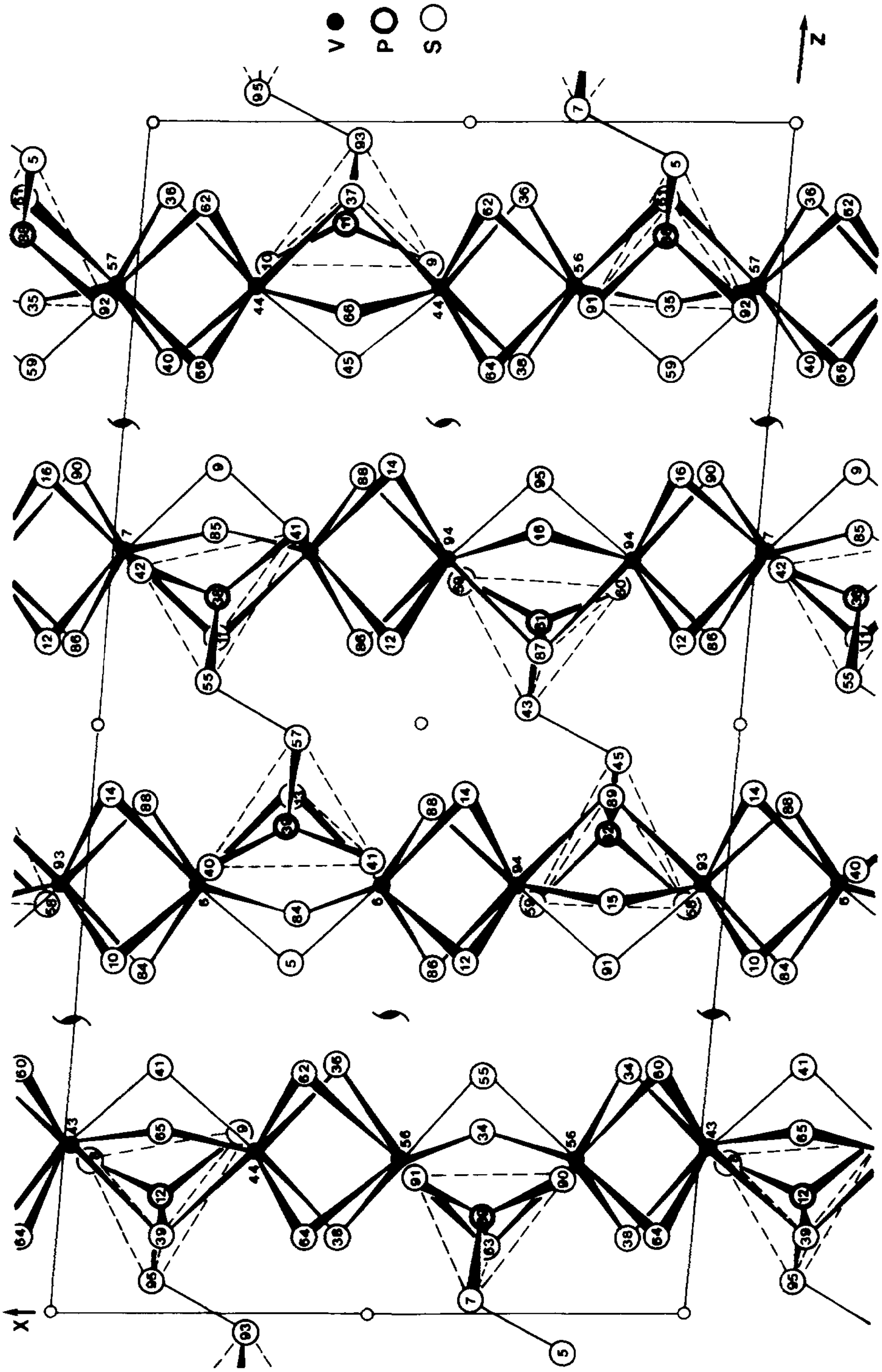

FIG. 2. Projection of PV_2S_{10} monoclinic structure along the *b* axis. Numbers represent fractional heights (×100) of the atoms.

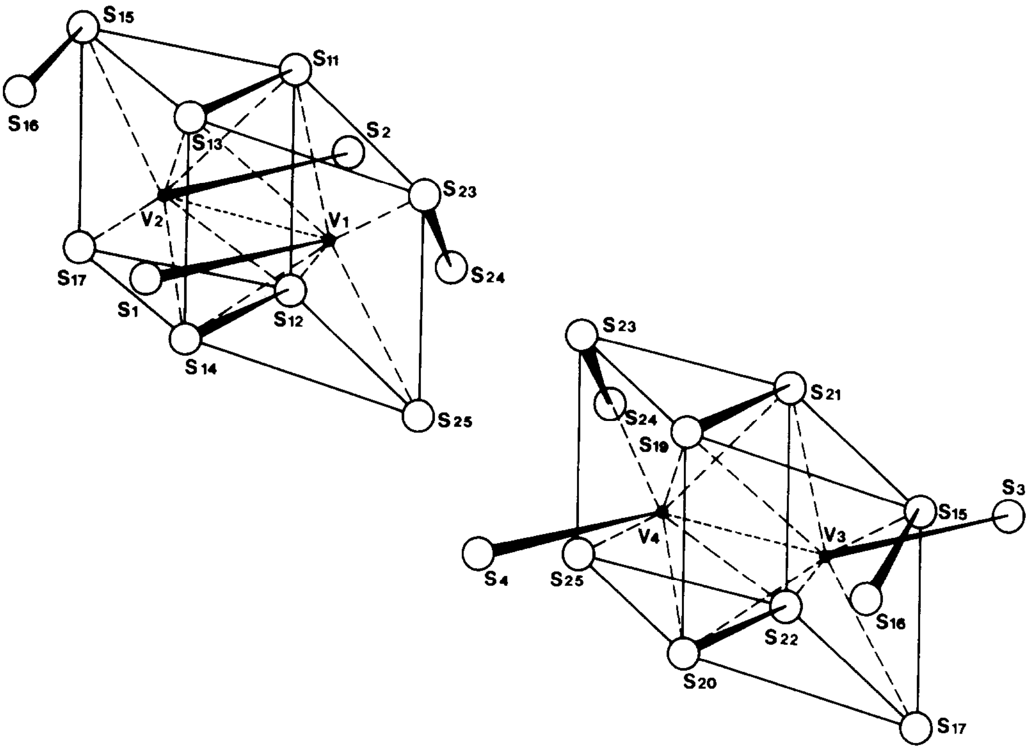

FIG. 3. Perspective view of both $[V_2S_{12}]$ units encountered in the PV_2S_{10} structure.

remarkable structural feature explains the very easy splitting of the single crystals and the typical hair-like look of cut crystal tips.

5. Physical Characterization of PV_2S_{10}

In the M–P–X compounds, phosphorus atoms in tetrahedral chalcogen coordination are often found as P^V cations as in $Cr^{III}P^VS_4$ (*10*), $P^V_{0.2}Cr^{III}Se_2$ (*1*) and $Ta^{IV}P^VS_6$ (*4*), for example, and as can be deduced from the transition metal oxydation state. We may assume the same behavior for PV_2S_{10} as the P–S distances agree well with P^V–S distance values in the $[PS_4]$ tetrahedra of the above phases. In one crystal cell, considering 28 sulfur pairs and 24 regular sulfur anions, one has the formula $P_8V_{16}(S_2)_{28}S_{24}$ for the phase, i.e., $P^V_2V^{IV}_4(S_2^{-II})_7S_6^{-II}$. Charge balance is thus achieved with V^{IV} cations and, indeed, the

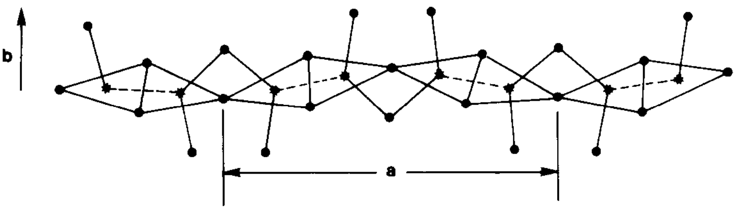

FIG. 4. Schematic drawing of a $[V_2S_9]_\infty$ chain constituting PV_2S_{10} framework.

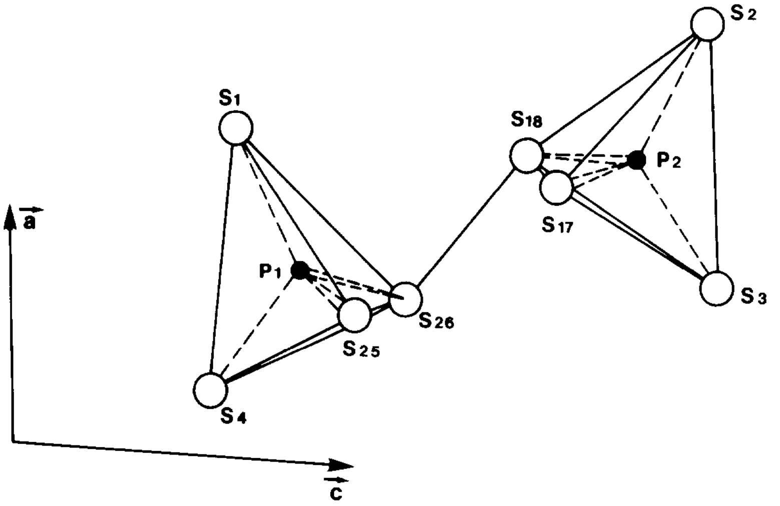

FIG. 5. Representation of a $[P_2S_8]$ unit bonding two $[V_2S_9]_\infty$ chains together.

TABLE IIIa

MAIN INTERATOMIC DISTANCES (Å) IN BOTH $[V_2S_{12}]$ UNITS[a]

V(1)–S(1)	2.592	V(2)–S(2)	2.578	V(3)–S(3)	2.563	V(4)–S(4)	2.593
–S(11)	2.434	–S(11)	2.390	–S(15)	2.472	–S(19)	2.382
–S(12)	2.385	–S(12)	2.415	–S(16)	2.480	–S(20)	2.404
–S(13)	2.376	–S(13)	2.417	–S(17)	2.537	–S(21)	2.425
–S(14)	2.401	–S(14)	2.387	–S(19)	2.431	–S(22)	2.398
–S(23)	2.456	–S(15)	2.475	–S(20)	2.383	–S(23)	2.467
–S(24)	2.484	–S(16)	2.481	–S(21)	2.381	–S(24)	2.495
–S(25)	2.541	–S(17)	2.536	–S(22)	2.406	–S(25)	2.537
Average V–S distance: 2.459							
V(1)–V(2)	2.853			V(3)–V(4)	2.850		
S(24)–S(23)	2.024	S(11)–S(13)	2.000	S(15)–S(16)	2.017	S(19)–S(21)	2.003
S(12)–S(14)	2.024	S(15)–S(16)	2.017	S(20)–S(22)	2.012	S(23)–S(24)	2.024
Average (S–S)$^{-\text{II}}$ distance: 2.015							
S(13)–S(14)	3.300	S(11)–S(12)	3.294	S(21)–S(15)	3.486	S(19)–S(15)	3.292
–S(1)	3.206	–S(2)	3.188	–S(22)	3.323	–S(20)	3.285
–S(23)	3.480	–S(24)	3.143	–S(3)	3.200	–S(16)	3.141
–S(15)	3.240	–S(15)	3.516	–S(23)	3.230	–S(23)	3.512
–S(16)	3.140	–S(23)	3.275	–S(24)	3.151	–S(4)	3.188
S(12)–S(2)	3.216	S(14)–S(25)	3.512	S(22)–S(25)	3.415	S(20)–S(17)	3.370
–S(25)	3.393	–S(17)	3.391	–S(24)	3.561	–S(4)	3.229
–S(17)	3.541	–S(16)	3.556	–S(17)	3.502	–S(25)	3.532
–S(24)	3.576	–S(1)	3.169	–S(3)	3.169	–S(16)	3.594
S(1)–S(23)	3.476	S(2)–S(15)	3.482	S(3)–S(15)	3.441	S(4)–S(23)	3.495
–S(25)	3.221	–S(17)	3.218	–S(17)	3.219	–S(25)	3.202
S(15)–S(17)	3.375			S(23)–S(25)	3.361		
Average S$^{-\text{II}}$–S$^{-\text{II}}$ distance: 3.344.							
S(24)–S(25)	2.995	S(16)–S(17)	2.972				

[a] Estimated standard deviation is 0.002 Å.

TABLE IIIb

MAIN S–S–S ANGLES IN BOTH $[V_2S_{12}]$ UNITS

Triangular faces	S(15)–S(11)–S(13)	65.35(7)	S(21)–S(15)–S(19)	34.23(5)
	S(11)–S(13)–S(15)	80.53(8)	S(19)–S(21)–S(15)	67.56(7)
	S(13)–S(15)–S(11)	34.13(5)	S(15)–S(19)–S(21)	78.21(8)
	S(13)–S(11)–S(23)	78.50(8)	S(21)–S(19)–S(23)	65.14(7)
	S(23)–S(13)–S(11)	67.22(7)	S(23)–S(21)–S(19)	80.61(8)
	S(11)–S(23)–S(13)	34.27(5)	S(19)–S(23)–S(21)	34.25(5)
	S(17)–S(12)–S(14)	69.01(7)	S(22)–S(17)–S(20)	33.98(4)
	S(14)–S(17)–S(12)	33.86(4)	S(20)–S(22)–S(17)	69.42(7)
	S(12)–S(14)–S(17)	77.13(7)	S(17)–S(20)–S(22)	72.60(8)
	S(14)–S(12)–S(25)	76.21(8)	S(22)–S(20)–S(25)	70.00(7)
	S(25)–S(14)–S(12)	69.77(7)	S(25)–S(22)–S(20)	76.39(7)
	S(12)–S(25)–S(14)	34.02(4)	S(20)–S(25)–S(22)	33.62(4)
S_2^{-II} pairs	S(17)–S(15)–S(16)	60.86(6)		
	S(24)–S(23)–S(25)	61.82(6)		
Rectangular faces	S(15)–S(13)–S(14)	89.23(5)	S(15)–S(21)–S(22)	90.51(5)
	S(13)–S(14)–S(17)	91.61(5)	S(21)–S(22)–S(17)	90.16(5)
	S(14)–S(17)–S(15)	85.50(5)	S(22)–S(17)–S(15)	89.37(5)
	S(17)–S(15)–S(13)	92.94(5)	S(17)–S(15)–S(21)	89.56(5)
	S(15)–S(11)–S(12)	90.99(5)	S(15)–S(19)–S(20)	88.96(5)
	S(11)–S(12)–S(17)	89.93(5)	S(19)–S(20)–S(17)	92.37(5)
	S(12)–S(17)–S(15)	89.23(5)	S(20)–S(17)–S(15)	86.17(5)
	S(17)–S(15)–S(11)	89.03(5)	S(17)–S(15)–S(19)	92.15(5)
	S(14)–S(13)–S(23)	90.55(5)	S(21)–S(23)–S(25)	93.77(5)
	S(13)–S(23)–S(25)	89.71(5)	S(23)–S(25)–S(22)	85.28(5)
	S(23)–S(25)–S(14)	89.01(5)	S(25)–S(22)–S(21)	91.15(5)
	S(25)–S(14)–S(13)	90.16(5)	S(22)–S(21)–S(23)	88.92(5)
	S(12)–S(11)–S(23)	88.61(5)	S(19)–S(23)–S(25)	89.00(5)
	S(11)–S(23)–S(25)	93.12(5)	S(23)–S(25)–S(20)	89.21(5)
	S(23)–S(25)–S(12)	85.58(5)	S(25)–S(20)–S(19)	89.88(5)
	S(25)–S(12)–S(11)	92.19(5)	S(20)–S(19)–S(23)	90.81(5)
	S(12)–S(14)–S(13)	89.48(7)	S(21)–S(19)–S(20)	90.34(8)
	S(14)–S(13)–S(11)	90.30(7)	S(19)–S(20)–S(22)	90.69(7)
	S(13)–S(11)–S(12)	90.06(7)	S(20)–S(22)–S(21)	89.11(7)
	S(11)–S(12)–S(14)	90.06(7)	S(22)–S(21)–S(19)	89.76(7)

V^{IV}–V^{IV} distance is found to be identical to that in $V^{IV}S_4$ (*7*) for d^1–d^1 vanadium pairs. Such a structural feature implies diamagnetism and semiconducting behavior for VS_4 and should have the same consequences on PV_2S_{10} electrical and magnetic properties.

Resistivity measured on single crystal with current applied along the fibers shows in effect PV_2S_{10} to be highly resistant with resistivity of about 10^9 Ω cm at 298 K. However, molar susceptibility measurements indicate a slight paramagnetism for the phase with room temperature $\chi_{\mathrm{mole}} = 120.10^{-6}$ emu. The occurrence of bonds between some $[S_2]^{-II}$ pairs and other S^{-II} anions, as pointed out in the structural study, must reduce the charges born by the anions, decreasing correspondingly those on the vanadium cations. Hence the likely occurrence of unpaired electrons on vanadium and the weak paramagnetism observed.

The variation of χ^{-1} versus temperature shows the magnetic susceptibility to follow a Curie–Weiss law in the 4.2–300 K range. From the curve slope, it is possible to cal-

TABLE IIIc

MAIN S-V-S ANGLES IN BOTH [V_2S_{12}] UNITS

Prisms	S(13)-V(1)-S(23)	92.12(7)	S(21)-V(3)-S(15)	91.83(6)
	S(11)-V(1)-S(23)	84.06(6)	S(21)-V(3)-S(17)	158.74(8)
	S(12)-V(1)-S(23)	142.73(7)	S(21)-V(3)-S(19)	49.19(7)
	S(14)-V(1)-S(23)	165.55(8)	S(21)-V(3)-S(20)	108.14(7)
	S(25)-V(1)-S(23)	84.50(6)	S(21)-V(3)-S(22)	87.92(7)
	S(25)-V(1)-S(11)	151.10(7)	S(19)-V(3)-S(20)	86.04(6)
	S(25)-V(1)-S(12)	87.00(6)	S(19)-V(3)-S(22)	106.39(7)
	S(25)-V(1)-S(13)	157.86(8)	S(19)-V(3)-S(15)	84.34(6)
	S(25)-V(1)-S(14)	90.53(6)	S(19)-V(3)-S(17)	150.29(7)
	S(12)-V(1)-S(11)	86.21(6)	S(20)-V(3)-S(22)	106.39(7)
	S(12)-V(1)-S(13)	108.12(7)	S(20)-V(3)-S(15)	143.25(7)
	S(12)-V(1)-S(14)	50.02(6)	S(20)-V(3)-S(17)	86.39(6)
	S(13)-V(1)-S(11)	49.11(6)	S(22)-V(3)-S(15)	165.24(7)
	S(13)-V(1)-S(14)	87.38(6)	S(22)-V(3)-S(17)	90.18(6)
	S(14)-V(1)-S(11)	50.02(7)	S(17)-V(3)-S(15)	84.72(6)
	S(15)-V(2)-S(17)	84.67(6)	S(21)-V(4)-S(19)	49.24(7)
	S(15)-V(2)-S(11)	92.55(6)	S(21)-V(4)-S(20)	106.05(7)
	S(15)-V(2)-S(12)	167.16(7)	S(21)-V(4)-S(22)	87.09(7)
	S(15)-V(2)-S(13)	82.93(6)	S(21)-V(4)-S(23)	82.63(6)
	S(15)-V(2)-S(14)	141.66(7)	S(21)-V(4)-S(25)	151.74(8)
	S(17)-V(2)-S(11)	157.66(7)	S(19)-V(4)-S(20)	86.68(7)
	S(17)-V(2)-S(12)	91.28(6)	S(19)-V(4)-S(22)	108.22(7)
	S(17)-V(2)-S(13)	151.16(7)	S(19)-V(5)-S(23)	92.79(6)
	S(17)-V(2)-S(14)	87.00(6)	S(19)-V(4)-S(25)	156.76(8)
	S(14)-V(2)-S(11)	108.11(7)	S(20)-V(4)-S(22)	49.55(6)
	S(14)-V(2)-S(12)	49.84(6)	S(20)-V(4)-S(23)	167.67(8)
	S(14)-V(2)-S(13)	86.75(6)	S(20)-V(4)-S(25)	91.24(6)
	S(13)-V(2)-S(11)	49.17(7)	S(22)-V(4)-S(23)	141.32(7)
	S(13)-V(2)-S(12)	105.85(7)	S(22)-V(4)-S(25)	87.54(6)
	S(12)-V(2)-S(11)	86.56(7)	S(23)-V(4)-S(25)	84.39(6)
Angles with capping S atoms	S(1)-V(1)-S(13)	80.25(7)	S(3)-V(3)-S(15)	86.21(6)
	S(1)-V(1)-S(14)	78.69(7)	S(3)-V(3)-S(17)	78.27(6)
	S(1)-V(1)-S(23)	86.99(7)	S(3)-V(3)-S(21)	80.58(7)
	S(1)-V(1)-S(25)	77.72(6)	S(3)-V(3)-S(22)	79.19(7)
	S(24)-V(1)-S(11)	79.43(6)	S(16)-V(3)-S(15)	48.08(5)
	S(24)-V(1)-S(12)	94.49(7)	S(16)-V(3)-S(17)	72.63(6)
	S(24)-V(1)-S(25)	73.15(6)	S(16)-V(3)-S(19)	79.53(6)
	S(24)-V(1)-S(23)	48.36(5)	S(16)-V(3)-S(20)	95.28(6)
	S(2)-V(2)-S(11)	79.75(7)	S(4)-V(4)-S(19)	79.58(7)
	S(2)-V(2)-S(12)	80.13(7)	S(4)-V(4)-S(20)	80.43(7)
	S(2)-V(2)-S(15)	87.11(6)	S(4)-V(4)-S(23)	87.35(7)
	S(2)-V(2)-S(17)	77.98(6)	S(4)-V(4)-S(25)	77.26(6)
	S(16)-V(2)-S(13)	48.04(5)	S(24)-V(4)-S(23)	48.13(5)
	S(16)-V(2)-S(13)	79.73(6)	S(24)-V(4)-S(25)	73.04(5)
	S(16)-V(2)-S(14)	93.82(7)	S(24)-V(4)-S(21)	79.62(6)
	S(16)-V(2)-S(17)	72.63(6)	S(24)-V(4)-S(22)	93.38(7)

culate the number of unpaired electrons (0.19 per vanadium). Considering then the 16 vanadium and 8 [S_3] groups of the cell, a negative charge of 3.6 is calculated for the trisulfur unit. Assuming a proportionnality between the sulfur–sulfur distances and the charge of the anions, with both extreme values of 2.015 and 3.344 Å a negative

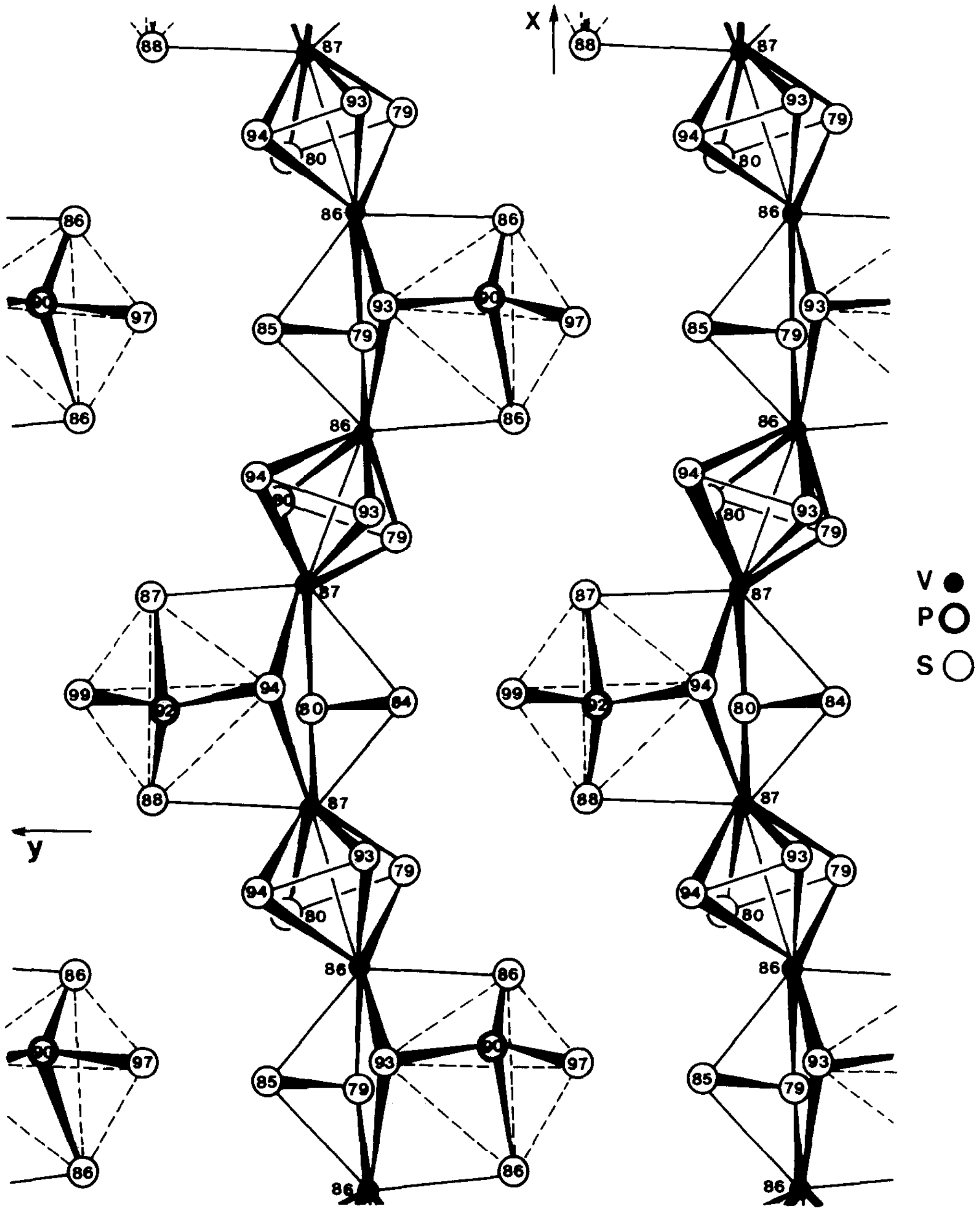

FIG. 6. Projection of PV_2S_{10} structure along the z axis. Only one basal chain is represented. Numbers correspond to fractional heights (×100) of the atoms.

charge of 3.4 is found to be born by the $[S_3]$ units. Both results are in reasonable agreement although such a reasoning corresponds to a very simple model indeed. It has, however, the advantage of recalling other one-dimensional situations like in $NbSe_3$ (*12*) or TaS_3 (*9*). In such compounds, more or less stretched (Se–Se) or

TABLE IV

MAIN DISTANCES (Å) AND ANGLES IN BOTH (P_2S_8) GROUPS[a]

P(1)–S(2)	2.012	P(2)–S(1)	1.993
–S(3)	2.006	–S(4)	2.003
–S(17)	2.034	–S(25)	2.037
–S(18)	2.124	–S(26)	2.130
Average P–S distance: 2.042			
S(26)–S(18)	2.075		
S(1)–S(4)	3.414	S(2)–S(3)	3.395
–S(26)	3.460	–S(17)	3.218
–S(25)	3.221	–S(18)	3.278
S(4)–S(25)	3.202	S(3)–S(17)	3.219
–S(26)	3.183	–S(18)	3.509
S(25)–S(26)	3.487	S(17)–S(18)	3.381
S(3)–P(1)–S(17)	105.68(10)	S(1)–P(2)–S(4)	117.39(10)
S(3)–P(1)–S(2)	115.33(10)	S(1)–P(2)–S(25)	106.12(10)
S(3)–P(1)–S(18)	116.29(10)	S(1)–P(2)–S(26)	114.07(10)
S(2)–P(1)–S(17)	105.35(10)	S(4)–P(2)–S(25)	104.88(10)
S(2)–P(1)–S(18)	104.80(10)	S(4)–P(2)–S(26)	100.69(10)
S(17)–P(1)–S(18)	108.80(10)	S(25)–P(2)–S(26)	113.58(9)

[a] ESD is equal to 0.002 Å.

TABLE V

SOME S–S DISTANCES OF THE VAN DER WAALS' GAP

S(23)–S(21)	3.877(2)	S(15)–S(11)	3.753(2)	S(24)–S(1)	3.748(2)
–S(19)	3.215(2)	–S(13)	3.228(2)	–S(4)	3.677(2)
–S(3)	3.685(2)	S(16)–S(11)	3.652(2)	S(13)–S(2)	3.814(2)
S(24)–S(19)	3.587(2)	S(19)–S(23)	3.877(2)	S(16)–S(2)	3.558(2)
S(11)–S(15)	3.753(2)	–S(24)	3.587(2)	–S(3)	3.646(2)
–S(16)	3.652(2)	–S(21)	3.752(2)	–S(18)	3.480(2)
–S(13)	3.750(2)	S(21)–S(23)	3.215(2)	S(19)–S(3)	3.696(3)
S(14)–S(15)	3.228(2)	–S(4)	3.998(2)		
–S(2)	3.725(2)	–S(19)	3.752(2)		
–S(2)	3.750(2)				

(S–S) anionic pairs control the electronic density on the neighbor metallic chains.

6. Conclusion

PV_2S_{10} is a new semiconducting one-dimensional phase made of [V_2S_9] chains, built from [V_2S_{12}] group in which are found the typical bicapped trigonal sulfur prisms already encountered in some niobium and tantalum chalcogenides (*4, 8, 9*). Two adjacent chains are bonded together by S_3P–(S–S)–PS_3 arrangements constituted by two [PS_4] tetrahedra sharing $[S_2]^{-II}$ pairs. Within the [V_2S_{12}] units, vanadium–vanadium links are found. Occurrence of bondings between $[S_2]^{-II}$ and S^{-II} anions alter the expected diamagnetism of PV_2S_{10} leading to weak paramagnetism. Only van der Waals' forces exist between the double chain and this very interesting feature, along with vanadium high oxydation state, make PV_2S_{10} a potential candidate for ions or molecules intercalation between chains.

After VPS_3 ($CdCl_2$ type) (*11*) and $P_{0.2}VS_2$ (CdI_2 type) (*2*), PV_2S_{10} is the third phase of the P–V–S diagram. We may notice that, with layered structure for both first phases, all the above compounds are of low dimensionality.

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