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$NaV_{1-x}P_2S_6$ ($x = 0.16$): A New Compound with Infinite Straight ($^1/_\infty$)$[V_{0.837}P_2S_6]^-$ Chains that Exfoliate Forming Gels

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The new 1D chalcogenophosphate material $NaV_{0.837(6)}P_2S_6$ has been synthesized and its structure determined by X-ray powder diffraction analysis. This compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.9677(3)$ Å, $b = 5.9059(2)$ Å, $c = 21.4537(8)$ Å, and $\beta = 92.962(2)°$ [$Z = 4$, $V = 881.66(8)$ Å^3]. The Rietveld refinement led to $R_p/R_{wp} = 0.0208/0.0271$ (for 94 parameters refined). The material is isostructural with 1D-$NaCrP_2S_6$ and contains infinite ($^1/_\infty$)$[V_{0.837(6)}P_2S_6]^-$ chains consisting of randomly occupied edge-sharing $[VS_6]$ octahedra defining zigzag ($^1/_\infty$)$[VS_4]$ ribbons that are capped by tetradendate $[P_2S_6]$ ethane-like groups linked to three successive $[VS_6]$ polyhedra. Because of the nonstoichiometry of the phase, the charge balance can be written as $Na^+(V^{4+})_{0.486}(V^{3+})_{0.351}(P^{4+})_2(S^{2-})_6$. $NaV_{0.837(6)}P_2S_6$ is soluble in strongly polar organic solvents such as *N*-methylformamide (NMF). The exfoliation of $NaV_{0.837(6)}P_2S_6$ in NMF leads to gels or to colored colloidal solutions with complex fluid behavior that depends strongly on concentration.

1. Introduction

A number of quaternary alkali (A) and transition metal (M) chalcogenophosphate with the crystal formula $A_wM_xP_yS_z$ (M = Cr, V)[1−4] have recently been prepared employing either the reactive flux method or the classical ceramic route from direct combination of the reagents in stoichiometric amounts. Structural analysis of these phases revealed the influence of the ratio $\tau = A/(M + P)$ on the dimensionality of the covalent network. Thus, 0D-$K_6Cr_2P_4S_{16}$, ($\tau = 1$) is composed of discrete $[Cr_2(PS_4)_4]^{6-}$ entities, and 1D-$A_3Cr_2P_3S_{12}$, (A = Na, K; $\tau = 0.6$) and 1D-$NaCrP_2S_6$, ($\tau = 0.33$) contain infinite $[Cr_2P_3S_{12}]^{3-}$ and $[CrP_2S_6]^-$ chains, respectively, whereas 2D-KMP_2S_7, (M = Cr, V; $\tau = 0.33$) is composed of $[MP_2S_7]^-$ layers. Also identified was 3D-$NaCrP_2S_6$, a metastable, allotopic form of $NaCrP_2S_6$. The anionic networks of all of these materials are stabilized by strong covalent bonds, and their overall structures are completed by weaker ionic interactions between the anionic network and the alkali metal cations.

A potentially interesting property of some low-dimensional compounds is their exfoliation in polar solvents. A prime example of this behavior is $LiMo_3Se_3$[5] and the transition metal thiophosphate compounds $KNiPS_4$[6] and $APdPS_4$.[7] These three compounds are composed of infinite anionic ($^1/_\infty$)$[Mo_3Se_3]$, ($^1/_\infty$)$[NiPS_4]$, and ($^1/_\infty$)$[PdPS_4]$ chains, respectively. Whereas the ($^1/_\infty$)$[NiPS_4]$ chains undergo autofragmentation under the action of the solvent to give rise to unprecedented discrete crown-shaped $[Ni_3P_3S_{12}]^{3-}$ anions,[8] the ($^1/_\infty$)$[PdPS_4]$ and ($^1/_\infty$)$[Mo_3Se_3]$ chains are maintained in solution,[8,9] inducing complex fluid and liquid crystal behavior, respectively. Because of the potentially interesting physical properties and the chemical reactivity of low-dimensional materials in solution, we recently embarked on a quest for new soluble alkali metal containing chainlike thiophosphates with magnetically active transition elements [i.e., V^{3+} (d^2, $S = 1$) and Cr^{3+} (d^3, $S = {}^3/_2$)]. Such systems are highly worthy of

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investigation because dilute nematic suspensions might be oriented and controlled by applying a magnetic or electric fields. In this paper, we report the preparation of a new mixed-valent compound, 1D-$NaV_{0.837(6)}P_2S_6$, its crystal structure, and its unusual exfoliation and gel forming properties in solution. It is noteworthy that gel formation among non-oxidic systems such as sulfide and chalcogenides is rare.

2. Experimental Section

Materials. All phases were handled in a drybox under nitrogen (O_2 and H_2O contents < 5 ppm). Na_2S_3 was prepared in liquid ammonia from a stoichiometric mixture of elemental sodium and sulfur (99.999%, Fluka).

Synthesis. For the preparation of $NaV_{0.837(6)}P_2S_6$, 0.1079 g (0.7 mmol) of Na_2S_3, 0.0773 g (1.5 mmol) of V (>99%, Aldrich), 0.0941 g (3 mmol) of P (red, Fluka), and 0.2190 g (6.8 mmol) of S (99.999%, Fluka) were thoroughly mixed and subsequently sealed under vacuum ($<10^{-2}$ Pa) in a silica tube. The reaction mixture was heated to 600 °C at a rate of 5 °C/h. The temperature was kept at 600 °C for 1 week and then decreased to room temperature at a rate of 5 °C/h. The resulting sample contained both dark needlelike crystals of $NaV_{0.837(6)}P_2S_6$ and dark platelike crystals of V_5S_8. An EDXS (energy-dispersive X-ray spectroscopy) analysis using a JEOL microscope (PGT-IMIX-PTS equipped JEOL-JSM5800LV) on a polished section of the sample indicated the composition $NaV_{0.8}P_{1.8}S_{5.4}$. The needles are not soluble in acetonitrile, dimethysulfoxide (DMSO), and dimethylformamide (DMF), but they are soluble in DMSO when 18-ether-6 or [2.2.2]cryptand is added and in pure *N*-methylformamide (NMF).

Structure Determination. *Data Collection.* As suitable crystals could not be found for X-ray structural determination, the $NaV_{0.837(6)}P_2S_6$ structure was refined from the X-ray diffraction powder pattern. This was possible because $NaV_{0.837(6)}P_2S_6$ is isostructural with the chromium derivative $NaCrP_2S_6$.[3] A powder sample with V_5S_8 as the only impurity was sieved at 50 μm and introduced, under a dry argon atmosphere, into a Lindemann capillary (0.1 mm in diameter). The powder pattern was recorded at room temperature on an INEL diffractometer using monochromatized Cu K$-$L$_2$ radiation (λ = 1.540 59 Å). This system was equipped with a CPS 120 detector in a Debye$-$Sherrer geometry.

Structure Refinement. The $NaV_{0.837(6)}P_2S_6$ structure refinement was carried out with Jana2000[10] software using powder diffraction data (see Supporting Information). The V_5S_8 impurity was simultaneously refined starting from the parameters found in the literature.[11] In a first step, a Le Bail analysis[12] of the diagram ($7 < 2\theta < 104$, excluded region $10 < 2\theta < 12.5$, $\Delta 2\theta$ step = 0.03, number of reflections = 1079) led to accurate cell parameters, peak shape (pseudo-Voigt), and approximate background (Chebyschev polynomials). Then, a Rietveld refinement[13] of the structure was carried out, starting from the $NaCrP_2S_6$ structural model ($P2_1/n$ space group, $Z = 4$).[3] Given the weak intensity of the powder pattern at high 2θ values, the isotropic displacement parameters (U_{iso}) of the thiophosphate group atoms and V and S atoms in V_5S_8 were constrained to be the same for each atomic species. The refinement of the atomic coordinates for all atoms and of the U_{iso} values of the V and P atoms of the thiophosphate of the sodium and vanadium compound led to values of $R_p = 0.0221$ and $R_{wp} = 0.0290$ for 92 refined parameters. Because of the high value of U_{iso} for V [$U_{iso} = 0.042(3)$ Å^2], its occupancy factor was refined. The occupancy decreased from 1 to 0.837(1) as U_{iso} dropped to 0.0089, a satisfactory value. Finally, by refining the U_{iso} values of the Na, P, and S atoms of the main phase, the residual factors converged to $R_p = 0.0208$ and $R_{wp} = 0.0271$. The impurity V_5S_8 was quantified at 10.26(17) wt %. Data collection parameters and refinement details for $NaV_{0.837(6)}P_2S_6$ are summarized in Table 1. Atomic coordinates and isotropic displacement parameters are given in Table 2. The final X-ray powder pattern with the Rietveld profile and difference diagram is given in Figure 1.

Table 1. Crystal, X-ray Data Collection, and Refinement Parameters

chemical formula	$NaV_{0.837(6)}P_2S_6$
molecular weight (g·mol^{-1})	319.99
crystal system	monoclinic
space group	$P2_1/n$
color	black purple
cell parameters	$a = 6.9677(3)$ Å
	$b = 5.9059(2)$ Å
	$c = 21.4537(8)$ Å
	$\beta = 92.962(2)°$
	$V = 881.66(8)$ Å^3
	$Z = 4$
half-width parameters	GV = 0.0070(10)
	GW = 0.0010 (2)
	LX = 0.00060(5)
	LY = 0.0009(2)
asymmetry parameters ($2\theta < 40°$)[a]	$S/L = 0.0290(5)$
	$H/L = 0.011\,808$
preferred orientation[b]	1.194(4)
reliability factors[c]	$R_p = 0.0208$
	$R_{wp} = 0.0271$
	$\chi^2 = 2.48$
refined parameters	94

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Table 2. Fractional Atomic Coordinates, Equivalent Isotropic Displacement Parameters (Å^2), and su's

atom	x	y	z	U_{iso}[a]
Na	0.4434(16)	0.869(3)	0.2810(6)	0.024(5)
V	0.5177(9)	0.755(2)	0.9584(4)	0.0089
P(1)	0.2891(11)	0.744(2)	0.1132(3)	0.006(2)
P(2)	0.5924(11)	0.745(2)	0.1358(4)	0.006(2)
S(1)	0.6811(12)	0.577(2)	0.0520(5)	0.0028(14)
S(2)	0.2739(13)	0.915(2)	0.0238(4)	0.0028(14)
S(3)	0.7695(11)	0.604(2)	0.9040(4)	0.0028(14)
S(4)	0.3404(13)	0.913(2)	0.8702(4)	0.0028(14)
S(5)	0.1450(11)	0.853(2)	0.1819(3)	0.0028(14)
S(6)	0.6710(10)	0.584(2)	0.2109(4)	0.0028(14)

[a] $U_{iso} = {}^1/_2\Sigma_i\Sigma_j U^{ij} a_i{}^* a_j{}^* a_i a_j$.

Electron Microscopy. Under a controlled atmosphere, $NaV_{0.837}P_2S_6$ powder was dissolved in NMF to form a 6.3×10^{-3} mol·L^{-1} colloidal solution. A droplet of the suspension containing chains (see below) was then deposited on a holey carbon coated electron microscopy grid. The sample was mounted into a Gatan 626 specimen holder and immediately transferred into a CM 30 Twin Philips electron microscope (HT = 300 kV, Cs = 2 mm) where the solvent was completely evaporated under a secondary vacuum ($P = 10^{-6}$ Pa). Electron microscopy studies on the residue were then carried out at room temperature.

3. Structure Description

$NaV_{0.84}P_2S_6$ is isostructural with $NaCrP_2S_6$ (Figure 2a). The difference lies only in the occurrence of vanadium vacancies inside the chains. $NaV_{0.837(6)}P_2S_6$ can be described as being composed of infinite ($^1/_\infty$)-$[V_{0.837(6)}P_2S_6]^-$ chains made of [VS_6] octahedra and [P_2S_6] ethane-like groups. The randomly occupied [VS_6] octahedra are linked to each other by edge sharing to form

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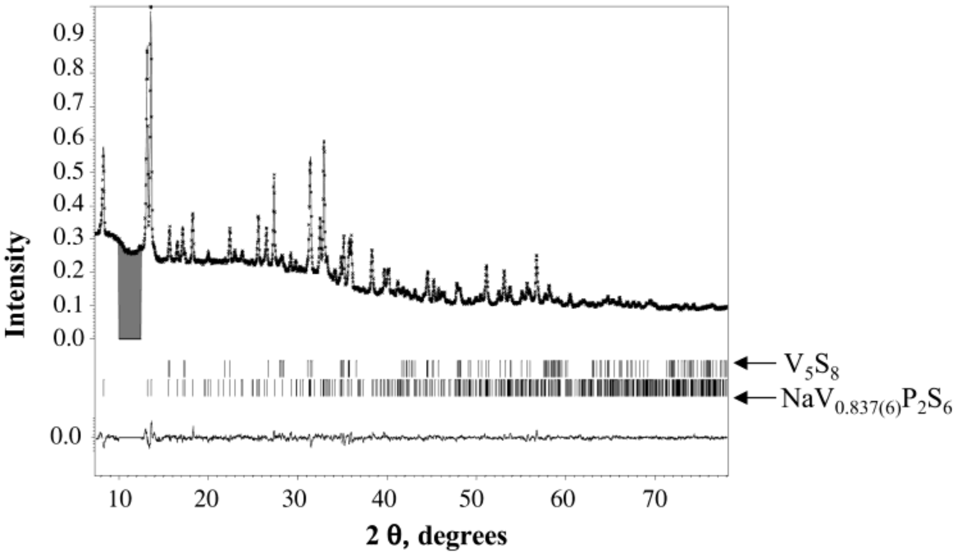

Figure 1. Observed (crossed line), calculated (solid line), and difference X-ray powder patterns obtained from the Rietveld refinement of $NaV_{0.837(6)}P_2S_6$. The gray zone corresponds to the excluded region between 10° < 2θ < 12.5°.

Table 3. Main Interatomic Distances (Å), Angles (°), Corresponding su's, andBond Valence Parameter (v_i)

VS_6 group		P_2S_6 group
distance	v_i[a]	distance
V−S(1) = 2.490(15)	0.495	P(1)−S(2) = 2.165(14)
V−S(1) = 2.403(18)	0.626	P(1)−S(3) = 2.123(18)
V−S(2) = 2.448(14)	0.554	P(1)−S(5) = 1.935(12)
V−S(2) = 2.451(18)	0.550	P(2)−S(1) = 2.170(15)
V−S(3) = 2.334(13)	0.754	P(2)−S(4) = 2.08(2)
V−S(4) = 2.395(14)	0.640	P(2)−S(6) = 1.926(14)
$\overline{V-S}$ = 2.42		$\overline{P-S}$ = 2.06
V−V = 3.52(2)		P(1)−P(2) = 2.144(11)
V−V = 3.42(2)		P(2)−P(1)−S(3) = 102.7(7)
V−V−V = 116.8(3)		P(2)−P(1)−S(5) = 111.8(5)
S(1)−V−S(2) = 87.4(4)		P(2)−P(1)−S(2) = 101.6(5)
S(1)−V−S(1) = 88.2(6)		S(3)−P(1)−S(5) = 110.6(6)
S(1)−V−S(3) = 94.9(6)		S(3)−P(1)−S(2) = 107.2(5)
S(1)−V−S(4) = 88.5(4)		P(1)−P(2)−S(1) = 97.5(5)
S(1)−V−S(2) = 88.1(4)		P(1)−P(2)−S(6) = 115.0(6)
S(1)−V−S(2) = 90.1(4)		P(1)−P(2)−S(4) = 102.2(7)
S(1)−V−S(3) = 85.3(4)		S(1)−P(2)−S(4) = 108.6(6)
S(2)−V−S(2) = 91.5(6)		S(1)−P(2)−S(6) = 112.8(8)
S(2)−V−S(4) = 87.6(5)		S(4)−P(2)−S(6) = 118.4(7)
S(3)−V−S(4) = 97.2(4)		

[a] $v_i = \exp[(R_i - d_i)/b]$.

zigzag $(^1/_\infty)[VS_4]$ infinite chains running along the *b* axis. These chains are completed by capping tetradendate ethane-like $[P_2S_6]^{4-}$ groups sharing edges with three successive $[VS_6]$ octahedra (Figure 2b). These anionic chains are separated from each other by the Na cations, located in sulfur five coordinate sites issued from three adjacent chains (Figure 3). The V−S, P−S, and Na−S distances range from 2.334(13) to 2.490(15) Å, from 1.926(14) to 2.170(15) Å, and from 2.800(19) to 3.04(2) Å, respectively, with mean values of $\overline{V-S}$ = 2.42 Å, $\overline{P-S}$ = 2.06 Å, and $\overline{NA-S}$ = 2.93 Å. (See Table 3.) Judging from Na^+ and $[P_2S_6]^{4-}$ ions,[14] the average oxidation state of the V atoms is 3.58, consistent with a mixture of V^{3+} and V^{4+} ions. An estimate of the oxidation state of the V atoms was made by calculating the V bond valence sum value from D. Brown's formula[15] using the V−S bond lengths; this yielded a mean valence of 3.62, in good agreement with the expected value. Therefore, the compound is expected to be paramagnetic (preliminary studies confirm this), and because of its semiconducting property,[16] a more descriptive formula is be $Na^+(V^{4+})_{0.486}(V^{3+})_{0.351}\square_{0.163}(P^{4+})_2(S^{2-})_6$.

The structure of $NaV_{0.837(6)}P_2S_6$ can be compared to those that of $AgMP_2S_6$ (M = Cr, V),[17] which where shown to exhibit interesting magnetic properties.[18] Indeed, the same $(^1/_\infty)[MP_2S_6]^-$ chains are present in $AgMP_2S_6$, but instead of being isolated as in $NaV_{0.837(6)}P_2S_6$, they are bridged covalently by Ag^+ ion to produce a layered structure. So far, the magnetic susceptibility of $NaV_{0.837(6)}P_2S_6$ remains uncertain because of the presence of paramagnetic V_5S_8 as an impurity.

4. Behavior in Solution

$NaV_{0.837(6)}P_2S_6$ needles are soluble in NMF ($\epsilon = 182$) but insoluble in DMSO ($\epsilon = 46$), acetonitrile ($\epsilon = 37.5$), and DMF ($\epsilon = 37$): the higher the dielectric constant of the solvent, the greater the ability of the inorganic species to dissolve. Nevertheless, dissolution in DMSO can be achieved by the addition of 18-crown-6 ether and/or [2.2.2]cryptand. These molecules encapsulate the alkali metal, favoring the physical separation of the fibers, decreasing the cohesive energy of the solid, and leading to full dispersion.

In NMF, $NaV_{0.837(6)}P_2S_6$ needles immediately swell and exfoliate to form a deep purple, homogeneous gel or a sol that is unstable in air. The border concentration between the gel and sol is located at about 6×10^{-2}

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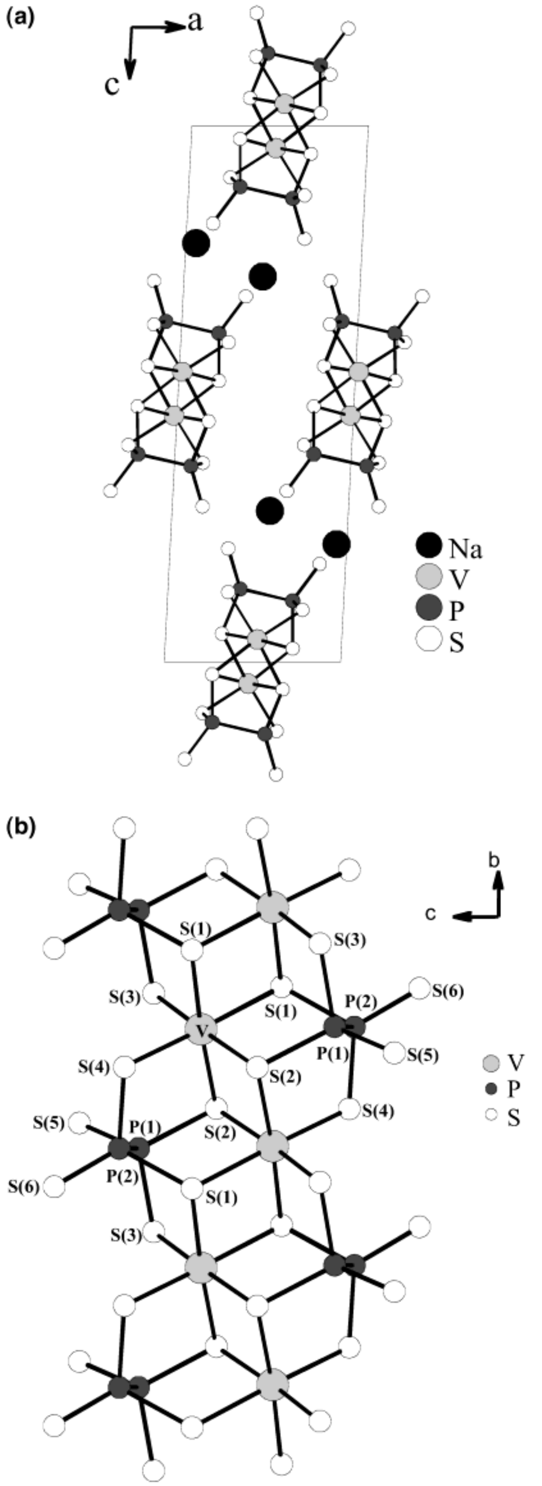

Figure 2. (a) View of the unit cell packing of the $NaV_{0.837(6)}P_2S_6$ structure along the *b* axis. (b) View of the $(^1/_\infty)[V_{0.837(6)}P_2S_6]^-$ chains running along the *b* axis. The $[VS_6]$ octaedra define an infinite zigzag chain built from edge [S(1)−S(1) or S(2)−S(2)] sharing. These $[VS_6]$ octaedra are capped on each side by $[P_2S_6]$ ethane-like groups.

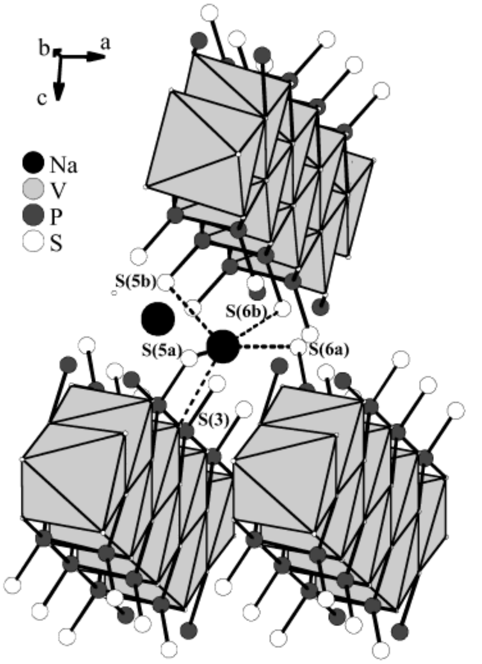

Figure 3. Perspective view of $NaV_{0.837(6)}P_2S_6$ structure. The $[VS_6]$ octahedra are represented by polyhedra. The sodium atoms are located in a sulfur pentagonal site formed by three neighbor chains. The sodium−sulfur distances are Na−S(5a) = 3.04(2) Å, Na−S(5b) = 2.897(14) Å, Na−S(6a) = 2.970(16) Å, Na−S(6b) = 2.800(19) Å, and Na−S(3) = 2.966(16) Å.

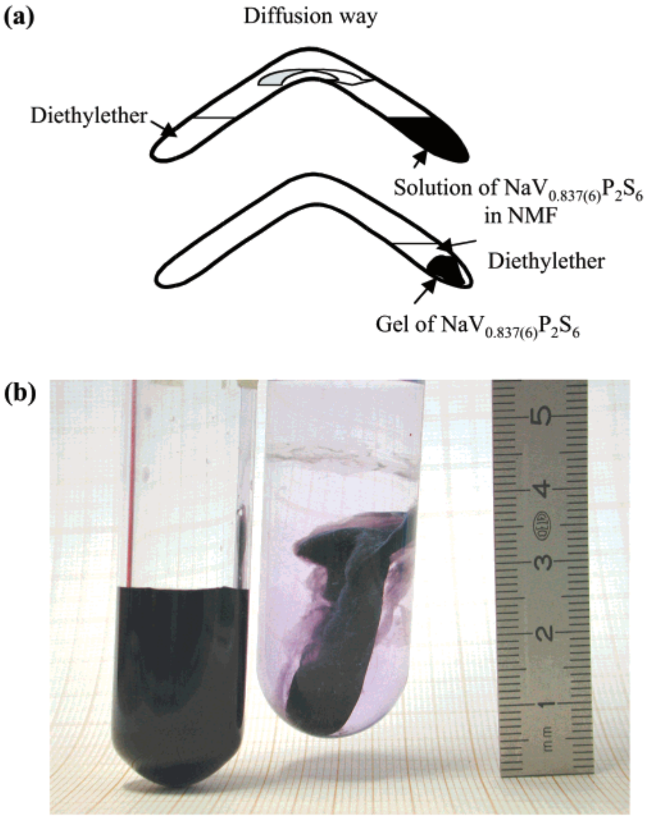

Figure 4. (a) Assembly allowing ether diffusion into a tube containing a $NaV_{0.837(6)}P_2S_6$/NMF solution. (b) On the left, a tube containing a solution of $NaV_{0.837(6)}P_2S_6$ in NMF (5 mL, *C* = 1.6×10^{-3} mol·L^{-1}). After the diffusion of 10 mL of ether into this tube, a gel is formed (right tube).

mol·L^{-1}. Another way to obtain a gel is to slowly diffuse ether vapor under nitrogen atmosphere at room temperature into a solution of $NaV_{0.837(6)}P_2S_6$ in NMF (Figure 4a). A purple gel is thus obtained by a lowering of the solubility of the solid. The gel formed in this way is surrounded by a limpid solution of ether (Figure 4b). Protected by a coating of ether, the gel is stable under nitrogen atmosphere over an extended period of time (several months). Following ether evaporation, the gel liquefies, returning to a sol.

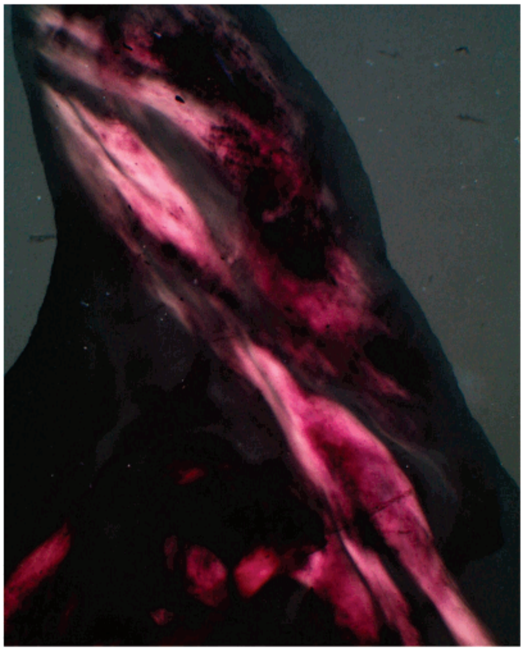

Figure 5. Induced transient birefringence observed by optical microscopy under polarized light (polarizers crossed) from a solution of $NaV_{0.837(6)}P_2S_6$ in NMF. The phenomenon is induced by flowing of the solution on a glass support (shear).

When observed by optical microscopy between crossed polarizers, fresh $NaV_{0.837(6)}P_2S_6$ colloidal solutions ($C \approx 1.3 \times 10^{-2}$ mol·L^{-1}) appear to be birefringent, suggesting the presence of anisotropically organized macromolecular entities in NMF. This birefringence slowly disappears, and within a few minutes, the solution appears isotropic at room temperature. If shear or stress is applied to this solution (with a spatula or under flow), a strong transient birefringence is immediately observed again (Figure 5), suggesting an induced reorientation of large anisotropic macromolecular fragments in solution. These fragments could be infinite $(^1/_\infty)[V_{0.837(6)}P_2S_6]^-$ chains resulting from the dissolution of $NaV_{0.837(6)}P_2S_6$ crystals in NMF. However, fragmentation into smaller chains cannot be ruled out. To evaluate the thermodynamic stability of these solutions over several months, regular withdrawals from a $NaV_{0.837(6)}P_2S_6$/NMF stock solution stored in a drybox were made. Both fresh or aged solutions exhibited transient birefringence. These observations are consistent with complex liquid-crystalline-like fluid behavior in solution and suggest that the $[V_{0.837(6)}P_2S_6]_n^{n-}$ chains remain nearly intact over long periods of time.

The existence of magnetically active anisotropic fragments containing V^{4+} (d^1) and V^{3+} (d^2) ions suggests the possible orientation of these links under a magnetic field. Several drops of $NaV_{0.837(6)}P_2S_6$/NMF ($C = 1.3 \times 10^{-2}$ mol·L^{-1}) were deposited on a microscope glass. Observed under polarized light, these solutions are birefringent under mechanical constraints. Unfortunately, attempts to align the fragments by bringing a samarium−cobalt magnet ($H = 1.5$ T) close to the solution revealed no birefringence.

To obtain further experimental evidence for the presence of long chains and chain fragments in the colloidal solutions, a transmission electron microscopy (TEM) analysis was performed on an evaporated solution of $NaV_{0.837(6)}P_2S_6$/NMF. TEM photographs evidenced flexible fragments assembled together to form ∼250-Å-wide bundles of chains several microns in length (Figure 6). These bundles turned out to be unstable under a focused electron beam, preventing the recording of any diffraction pattern. Nevertheless, the composition was maintained at nearly $V_{0.837}P_2S_6$, suggesting that the chemical integrity of the chains was conserved in solution and after evaporation. An isolated $(^1/_\infty)[V_{0.837(6)}P_2S_6]$ chain would have a 9.2 × 4 Å cross section, which suggests that the observed bundles are constructed from about 20 chains. Attempts to observe individual chains by introducing a large amount of [2.2.2]cryptand into a 2.5×10^{-3} mol/L $NaV_{0.837(6)}P_2S_6$/NMF sol were unsuccessful.

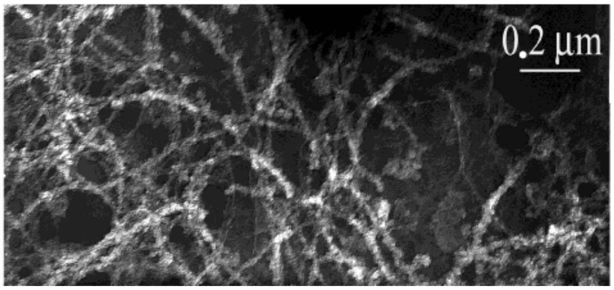

Figure 6. TEM micrograph of an evaporated solution of $NaV_{0.837(6)}P_2S_6$/[2.2.2]cryptand in NMF. The sample was prepared by directly depositing one drop of the NMF solution ($[NaV_{0.837(6)}P_2S_6] = 2.5 \times 10^{-3}$ mol·L^{-1}) onto a carbon grid and drying the drop under secondary vacuum ($P = 10^{-6}$ Pa).

5. Conclusion

The new strongly anisotropic 1D compound $NaV_{0.837(6)}P_2S_6$ exfoliates in highly polar solvents and gives rise to sols and gels in which likely $(^1/_\infty)[V_{0.837(6)}P_2S_6]^-$ anisotropic fragments are maintained. These fragments, which are directly observable by TEM, exhibit complex fluid behavior and transient birefringence phenomena. It is interesting to point out that $NaCrP_2S_6$ is also soluble in strongly polar solvents such as NMF.[19] At this stage, one might wonder what the role of the transition element is in the dissolution process and whether the exfoliation properties of these thiophosphates are related to the partial occupancy of the d orbitals of V and Cr. Future studies will attempt to address these points.

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Supporting Information Available: Data from crystal structure refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Posting. This article was originally published on 5/23/03 without the Supporting Information (SI). The SI was added and the article was reposted on 5/28/03.

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