Inorganic Chemistry

Scandium Selenophosphates: Structure and Properties of $K_4Sc_2(PSe_4)_2(P_2Se_6)$

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S Supporting Information

ABSTRACT: The new compound $K_4Sc_2P_4Se_{14}$ was synthesized via the polychalcogenide flux method. It crystallizes in the space group C2/c, and the structure is composed of $1/\infty[Sc_2P_4Se_{14}^{4-}]$ chains that are separated by K^+ cations. The structural motif features two $[PSe_4]^{3-}$ units and one $[P_2Se_6]^{4-}$ unit bridging the Sc centers and has not been reported for any other compound. The $1/\infty[Sc_2P_4Se_{14}^{4-}]$ chains pack in a crosshatched pattern perpendicular to the *c* axis of the crystal, forming channels for half of the K^+ atoms while the other half occupy empty space between the chains. The orange-yellow crystals of $K_4Sc_2P_4Se_{14}$ are air-sensitive and gradually turn red over the course of a couple hours. The band gap of the phase is 2.25(2) eV, and Raman spectroscopy shows the symmetric stretches of the selenophosphate groups to be at 231 and 216 cm⁻¹ for the $[PSe_4]^{3-}$ and $[P_2Se_6]^{4-}$ units, respectively. Solid-state ³¹P MAS NMR of



 $K_4Sc_2P_4Se_{14}$ shows two prominent peaks at 11.31 and -23.07 ppm and one minor peak at -106.36 ppm, most likely due to degradation of the product or an unknown second phase.

INTRODUCTION

Alkali- and rare-earth-metal-containing chalcophosphates have extremely varied crystal structures. These are a result of the diversity of selenophosphate ligands available^{1,2} and, to a greater extent, the identity of the rare-earth metal that is coordinated in the solid.^{1e,h,3} In the case of the lanthanides, the larger coordination sphere of the metal centers further contributes to the variety of structures that are possible in this class of compounds. One of note is $KSmP_2S_7$, which has intriguing layers of $[SmP_2S_7^-]$ that snake up and down in the [001] direction.⁴ Another example is LiEuPSe₄, which has channels of Li⁺ cations.² It is important to note that very little research has been done on such compounds, $l^{1a,b,h,k,2a,b,d,3-5}$ and physical property analysis has only been done on about half of the few compounds that have been discovered. $l^{1a,b,h,k,2b,d,d,4,5}$

Scandium and yttrium are not lanthanides but are, nonetheless, similar to them. Of the rare-earth elements, Y is most similar to Sc in its chemistry. There are only a few quaternary yttrium selenophosphates.^{2b,6} KYP₂Se₆, for example, contains sheets composed of Y³⁺ centers that are bridged by $[P_2Se_6]^{4-}$ units. These infinite sheets are then separated by the K⁺ ions. The compound has a band gap of around 2.75 eV and exhibits no magnetic activity, which makes sense because of the d⁰ metal centers.

It is unusual how little to no research has been done on scandium in this category of compounds. To date, only two known scandium-containing quaternary chalcophosphates exist: $AgScP_2S_6^{-7}$ and its selenium analogue, $AgScP_2Se_6^{-2e}$ The compounds have two-dimensional (2D) sheets wherein octahedrally coordinated Sc is bridged by $[P_2Se_6]^{4-}$ units. In

both compounds, Ag^+ ions incorporate into the sheets themselves instead of positioning themselves between the layers.⁷

Here we report the new compound $K_4Sc_2P_4Se_{14}$ (or $K_2ScP_2Se_7$ empirically), composed of chains of $1/_{\infty}[Sc_2P_4Se_{14}^{4-}]$, which was synthesized from a flux-containing reaction. Each chain has two distinct selenophosphate ligands bonded to the metal: $[PSe_4]^{3-}$ units that form $Sc_2P_2Se_8$ clusters and $[P_2Se_6]^{4-}$ units that bridge the $Sc_2P_2Se_8$ clusters along the chain direction. Thus, a more precise formula is $K_4Sc_2(PSe_4)_2(P_2Se_6)$. Other examples of compounds containing two types of selenophosphate ligands exist, such as $K_4Ti_2(P_2Se_9)_2(P_2Se_7)$ and $K_3Ru(P_3Se_4)(P_2Se_6)$, but they are quite rare. ^{1c,i}

To the best of our knowledge, this is the first report of an alkali-metal and scandium-containing chalcophosphate to date, and we could find no reported compounds with a similar chain structure. Other quaternary rare-earth-metal selenophosphates have similar compositions, but they consist of either 2D sheet substructures or a three-dimensional network.^{1k,2d,Sa,c}

EXPERIMENTAL SECTION

Reagents. All reagents were used as obtained from the specified supplier: diethyl ether (ACS grade, BDH Chemical, Leicestershire, U.K.); *N,N*-dimethylformamide (DMF; ACS grade, BDH Chemical, Leicestershire, U.K.); red phosphorus powder (99%, Sigma-Aldrich, St. Louis, MO); potassium metal (98%, Sigma-Aldrich, St. Louis, MO); scandium metal powder (99.9%, Alfa Aesar, Ward Hill, MA); selenium

Received: March 2, 2016

pellets (99.99%, Sigma-Aldrich, St Louis, MO). K₂Se was prepared by the reaction of stoichiometric amounts of potassium and selenium in liquid ammonia as described elsewhere.⁸ P₂Se₅ was prepared by the stoichiometric reaction of the elements in a 13 mm evacuated fused-silica tube at 460 °C for 48 h as described elsewhere.^{1e}

Synthesis. $K_4Sc_2P_4Se_{14}$. A mixture of 0.157 g (1.0 mmol) of K₂Se, 0.011 g (0.25 mmol) of scandium, 0.228 g (0.5 mmol) of P_2Se_5 , and 0.079 g (1.0 mmol) of selenium was added to a carbon-coated fusedsilica tube with an outer diameter of 9 mm, an inner diameter of 7 mm, and a length of 20 cm inside a nitrogen-filled glovebox. The tube was sealed under vacuum and subjected to the following heating profile: the reaction mixture was heated to 500 °C in 7 h and remained at that temperature for 24 h. The reaction was then cooled to 350 °C in 24 h and then cooled to room temperature in 1 h. The remaining flux in the ingot was dissolved in dinitrogen-degassed DMF, replacing the DMF every 10 min until the solvent remained clear, yielding orange-yellow, needlelike crystals of K4Sc2P4Se14, which became a bright-yellow powder when crushed. Energy-dispersive X-ray spectroscopy (EDS) analysis on several crystals gave an average stoichiometry of K4.0Sc2.0P4.4Se8.8 (normalized for scandium). The crystals were airsensitive and were stored in a glovebox to prevent oxidation.

Single-Crystal X-ray Crystallography. Data collection was performed on a STOE IPDS II diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) operating at 50 kV and 40 mA at 293 K. The crystal was coated in superglue on the mounting needle to prevent it from oxidizing in air. The crystal was then collected under a flow of nitrogen gas. Integration and numerical absorption corrections were performed on the structure using *X-AREA*, *X-RED*, and *X-SHAPE*.⁹ The structure was solved using direct methods and refined by full-matrix least squares on F^2 using the *SHELXTL* program package.¹⁰

Powder X-ray Diffraction (PXRD). A silicon-calibrated CPS 120 INEL powder X-ray diffractometer (Cu K α graphite-monochromatized radiation) equipped with a position-sensitive detector operating at 40 kV and 20 mA was used to collect PXRD data on ground crystalline samples of the product with a flat sample geometry. Samples were covered in paratone oil to prevent oxidation during measurement. The *Visualizer* program within *FindIt* was used to generate simulated patterns using the crystallographic information file (CIF) of the refined structure.

Scanning Electron Microscopy (SEM). A Hitachi S-3400 scanning electron microscope equipped with a PGT energy-dispersive X-ray analyzer was used to acquire images and semiquantitative EDS analyses. Spectra were collected using an accelerating voltage of 25 kV and an accumulation time of 60 s.

Solid-State ³¹**P Magic Angle Spinning (MAS) NMR.** ³¹**P** MAS NMR spectra were collected using a Varian VNMRS 400 MHz spectrometer. NH₄H₂PO₄ (δ = 0.8 ppm) was used as a reference for chemical shifts. Pure samples of K₄Sc₂P₄Se₁₄ were loaded into a 5 mm airtight zirconia rotor in a glovebox, and experiments were performed using a pulse width (pwx90) of 3.5 μ s and a relaxation delay of 5 min. A total of 1024 scans were collected for K₄Sc₂P₄Se₁₄, with a spin rate of 10000 rpm.

Solid-State UV–Vis Spectroscopy. A Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer was used to collect diffuse-reflectance spectra in the range of 200–2500 nm. The instrument was equipped with an integrating sphere and controlled by a personal computer. BaSO₄ was used as a standard and set to 100% reflectance. Samples were prepared by quickly placing the ground crystalline products on a bed of BaSO₄ in air. Collected reflectance data were converted to absorbance according to the Kubelka–Munk equation $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, *S* is the scattering coefficient, and *R* is the reflectance.

Raman Spectroscopy. Raman spectra of ground crystalline samples were collected on a DeltaNu Advantage NIR spectrometer equipped with a CCD detector. The beam source was emitted from a diode laser with 785 nm radiation. The samples were loaded into borosilicate glass capillaries for measurement in a glovebox and sealed with clay. A maximum power of 60 mW and a beam diameter of 35 μ m were used. The spectrum was collected using an integration time of 10 s.

Differential Thermal Analysis (DTA). Experiments were performed using a Shimadzu DTA-50 thermal analyzer. Ground crystalline samples (~20 mg) were sealed under vacuum (~ 10^{-4} mbar) in a fused-silica ampule. A similar amount of Al₂O₃ was sealed in a separate ampule under vacuum and used as a reference. The samples were heated and cooled at a rate of 5 °C/min to a maximum temperature of 600 °C.

RESULTS AND DISCUSSION

Synthesis. The synthesis of $K_4Sc_2P_4Se_{14}$ was relatively easy via the flux synthesis method because it appears to form as a single phase and the flux dissolved readily in DMF. This is true as long as a ratio of 4:1:2:4 $K_2Se/Sc/P_2Se_5/Se$ is used. The compound would not form when a direct combination reaction was attempted, forming only KPSe₆ and $K_2P_2Se_6$.

 $K_4Sc_2P_4Se_{14}$ is air- or water-sensitive and will quickly oxidize in around 30 min, turning redder as it is exposed to ambient air and eventually turning to a black powder. This is most likely due to the hard nature of the hard Lewis acid Sc^{3+} center, which would much rather bond to the hard O of water than the soft Se in the compound. $K_4Sc_2P_4Se_{14}$ is also very weakly diffracting, so PXRD of the sample under paratone oil yielded only an amorphous background (see the Supporting Information).

EDS was done on the oxidized samples, yielding seemingly random compositions depending on the point observed. On average, the composition of the oxidized samples was rich in O, Se, and K and deficient in Sc. PXRD of the fully oxidized samples was also done, and elemental Se peaks along with heavily shifted $K_4Sc_2P_4Se_{14}$ peaks were observed (see the Supporting Information).

Crystal Structure Description. $K_4Sc_2P_4Se_{14}$ crystallizes in the C2/c (No. 15) space group, in the 2/m Laue class, and is composed of $1/\infty[Sc_2P_4Se_{14}^{4-}]$ chains separated by K⁺ cations. See Table 1 for crystallographic data. The chains are composed of Sc_2P_2Se_8 clusters bridged by $[P_2Se_6]^{4-}$ units (Figures 1 and 2). This chain structure has not been previously reported to the best of our knowledge, but it is most similar to that of Ag_3Y(PSe_4)_2.⁶ Unlike $K_4Sc_2P_4Se_{14}$, Ag_3Y(PSe_4)_2 lacks the $[P_2Se_6]^{4-}$ unit and instead bridges every metal center with two $[PSe_4]^{3-}$ units. In $K_4Sc_2P_4Se_{14}$, the two Sc centers must be 3+ in order to balance the 4- charge of the $[P_2Se_6]^{4-}$ unit and the 6- charge of the two $[PSe_4]^{3-}$ units. The final 4- charge of the chain is balanced by the four K⁺ cations present.

It is good to note here that the ratio of the maximum/ minimum residual density of the solved structure is a bit large at 2.67. However, this can be accounted for by some slight disorder in the position on the terminal Se atoms on the $[P_2Se_6]^{4-}$ (Se6) and $[PSe_4]^{3-}$ (Se3) units as well as K1, which is normal for such compounds. This disorder is expressed by their larger than usual thermal ellipsoids.

The d^0 Sc centers are in a distorted octahedral coordination environment, which is most likely due to second-order Jahn– Teller distortion. Despite this, the compound as a whole is centrosymmetric because any distortion of one Sc in the Sc₂P₂Se₈ cluster is perfectly mirrored by the other Sc in the cluster, effectively canceling out any polar moments. The chains themselves pack in a crosshatched pattern when viewed along the [001] direction. This pattern forms channels that are filled by atom K2, while K1 is positioned elsewhere between the chains (Figure 2c).

In the compound, there are five distinct bonding environments for the Se atoms: two of which are part of the $[P_2Se_6]^{4-}$ unit and three of which are in the $[PSe_4]^{3-}$ units. Of the six Se

Table	1.	Crystallographic	Refinement Details	of $K_4Sc_2P_4Se_{14}$
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	compound	1
	empirical formula	$K_4Sc_2P_4Se_{14}$.
	fw, g/mol	737.82
	wavelength, Å	0.71073
	habit	needle
	color	orange-yellow
	cryst syst	monoclinic
	space group	C2/c
	a, Å	22.668(5)
	b, Å	6.815(2)
	c, Å	19.828(4)
	β , deg	113.91(3)
	<i>V</i> , Å ³	2800(1)
	Ζ	8
	ρ , g/cm ³	3.500
	μ , mm ⁻¹	19.499
	F(000)	2616
	$ heta_{ m max}$, deg	34.87
	reflns collected	21264
	R _{int}	0.0991
	no. of param	109
	refinement method	full-matrix least squares on F^2
	GOF	1.242
	final R indices [> $2\sigma(I)$], R1/wR2 ^a	0.0672/0.1363
	R indices (all data), R1/wR2 ^a	0.0842/0.1432
F	$P_1 = \sum E = E / \sum E w P_2$	$- \left[\sum \left[w(E ^2 - E ^2)^2 \right] \right]$

^aR1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. wR2 = $[\sum [w(|F_o|^2 - |F_c|^2)^2] / \sum [w(F_o^2)^2]^{1/2}]$ and calc $w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 1.2737P]$, where $P = (F_o^2 + 2F_c^2)/3$.



Figure 1. (a) Chain structures of $[Sc_2P_4Se_{14}]^{4-}$ and (b) $K_4Sc_2P_4Sc_{14}$ along the [010] direction (with labeled atoms).

atoms in $[P_2Se_6]^{4-}$, there are four that are bonded to both Sc and P (Se1 and Se2) and two that are bonded only to the P atom (Se3). Of the Se atoms in the $[PSe_4]^{3-}$ group, there are two that are monodentate to the Sc atom (Se4 and Se7), one that is bridging two Sc centers (Se5), and one that does not bond to the Sc atom (Se6).

Concerning $[P_2Se_6]^{4-}$, the Se-Sc distance is 2.668(2)– 2.677(2) Å. For the Se atoms in the $[PSe_4]^{3-}$ group, the Sc-Se bond distance is 2.730(2)–2.756(2) Å for Se5 and 2.679(2)– 2.699(2) Å for Se4 and Se7. The Sc-Sc distance is a



Figure 2. (a) [110], (b) [1–10], and (c) [001] directions. The view along the [110] and [1-10] directions reveals the crosshatched orientation of the chains within the unit cell, while the view along the [001] direction reveals the channels in which atom K2 resides.

nonbonding 3.942(2) Å. Between chains, the nearest interchain separation is between Se3 and Se6 with a distance of 3.748(2) Å. This is just below double the ionic radius of Se²⁻ (1.84–1.9 Å),¹¹ meaning there should be slight interchain interactions contributing to the electronic structure.

Thermal Properties. DTA of $K_4Sc_2P_4Se_{14}$ showed no peaks, either endothermic or exothermic, up to 600 °C. The sample solidified from a powder into a solid agglomerate and changed color from yellow to brown after heating, so it is puzzling that no thermal transitions were observed in the DTA signal. The PXRD pattern of the sample after DTA was unchanged, yielding only an amorphous background under paratone oil.

Optical Absorption Spectroscopy. The band gap of $K_4Sc_2P_4Se_{14}$ was measured to be 2.25(2) eV, which matches its orange-yellow color (Figure 3). Because of the large band gap



Figure 3. Absorption spectrum of $K_4Sc_2P_4Se_{14}$. The band gap was found to be around 2.25(2) eV. The sample was ground in the glovebox and quickly analyzed rapidly in air to prevent oxidation.

compared to those of other selenophosphates, this compound could be useful for study in third harmonic generation because a larger band gap is needed in order to prevent absorption processes. Measurement of the band gap was done in air, so there is a possibility that the compound began to oxidize during the measurement. If so, the expected band gap would be higher than that of the measured one as the compound turns more red in color with increased air exposure. As a result, the actual band gap of $K_4Sc_2P_4Se_{14}$ could actually be slightly greater than 2.25 eV.

Solid-state Raman spectroscopy was performed on $K_4Sc_2P_4Se_{14}$, yielding the spectra seen in Figure 4. The



Figure 4. Raman spectrum of K₄Sc₂P₄Se₁₄.

symmetric stretch of the $[PSe_4]^{3-}$ unit can be found at 231 cm⁻¹, while the asymmetric stretch is located at 438 cm^{-1.2d} Comparing the symmetric and asymmetric stretches of K₄Sc₂P₄Se₁₄ to those of other $[PSe_4]^{3-}$ containing rare-earth metals (237 and 443–454 cm⁻¹, respectively),^{2d} this compound has lower-energy stretching vibrations, suggesting slightly weaker P–Se bonds. This is perhaps due to the relatively hard and electronegative nature of the Sc³⁺ centers, which would draw electron density from the $[PSe_4]^{3-}$ units into the Se–Sc bonds. Other similar compounds also compare well with the measured Raman spectra.¹² The bending modes of $[PSe_4]^{3-}$ can also be determined by analogy to be at 143 and 178 cm^{-1.2d} The P–P stretch of the $[P_2Se_6]^{4-}$ group can be found at 216

The P–P stretch of the $[P_2Se_6]^{4-}$ group can be found at 216 cm⁻¹, which matches well to the P–P stretch at 217 cm⁻¹ of Sn₂P₂Se₆, which also contains the $[P_2Se_6]^{4-}$ unit.^{2f} The bending modes of the $[P_2Se_6]^{4-}$ unit are most likely at 114 and 156 cm⁻¹, while the other stretching modes can be found at 266, 372, 462, and 471 cm⁻¹.^{1h,2f,13} All peaks except for the signal at 402 cm⁻¹ could be assigned to the bending and stretching frequencies of the selenophosphate groups by analogy.¹³ This peak at 402 cm⁻¹ is most likely another asymmetric stretching group of either the $[P_2Se_6]^{4-}$ or $[PSe_4]^{3-}$ group. See Table 2 for a list of the categorized Raman stretches and bends.

Solid-State ³¹**P MAS NMR.** Solid-state ³¹**P** MAS NMR of $K_4Sc_2P_4Se_{14}$ shows two prominent peaks at 11.31 and -23.07

ppm (see Figure 5), which correspond to the P in the $[P_2Se_6]^{4-}$ and $[PSe_4]^{3-}$ units, respectively. Both peaks have an integration



Figure 5. Solid-state ³¹P MAS NMR of $K_4Sc_2P_4Se_{14}$. Two peaks at 11.31 and -23.07 ppm correspond to the $[PSe_4]^{3-}$ and $[P_2Se_6]^{4-}$ units, respectively. A minor impurity peak can be found around -106.4 ppm, and slight decomposition of the compound results in broadness and extra peaks between 5 and -15 ppm.

of approximately 1, which should be the case. It is also important to note a small peak at -106.36 ppm, which is either from a minor unknown second phase or partial oxidation of the compound. Seeing as no second unknown phases could be found using SEM/EDS, partial oxidation of the compound is more likely to be the source of this peak. The broadness observed between the peaks at 11.31 and -23.07 ppm is probably due to partial decomposition of the compound over the course of the measurement or in storage.

The peaks of the P atom match well with known ³¹P NMR peak positions. Compared to that of the similar onedimensional compound KNb_2PSe_6 (-8.32 ppm),¹⁴ the peak location in K₄Sc₂P₄Se₁₄ (-23.07 ppm) is more negative and therefore more shielded. This makes sense because Nb⁴⁺ would draw electron density from the $[PSe_4]^{3-}$ unit, shielding the P atom less compared to the Sc3+ center. The peak from the $[P_2Se_6]^{4-}$ unit is close to that of the peak location in Pb₂P₂Se₆ $(29.1 \text{ ppm})^{15}$ although it is more shielded comparatively. Most other $[P_2Se_6]^{4-}$ -containing compounds have even more positive resonance peaks. $Rb_2CdP_2Se_6$, for example, has a peak at around 62.0 ppm.¹⁵ The reason that the P atoms in $K_4Sc_2P_4Se_{14}$ are so shielded may be related to the bonding configuration of the $[P_2Se_6]^{4-}$ groups to the metals. In the Pb and Cd cases, all six Se atoms are bonded to the metal centers, whereas in the scandium compound, only four Se atoms are bonded. As a result, less electron density can be drawn away from the ligands to the metals, which makes the ³¹P NMR peak in the scandium compound have a smaller value.

CONCLUSIONS

The $K_4Sc_2P_4Se_{14}$ compound forms via flux synthesis and adopts a new structure with unique chains of

Table 2. Raman Shifts of K₄Sc₂P₄Se₁₄ Sorted According to Which Bending and Stretching Modes of Each Ligand They Can Be Attributed

	[PSe ₄] ^{3–} symmetric stretch	[PSe ₄] ^{3–} asymmetric stretch	[PSe ₄] ^{3–} bend	[P ₂ Se ₆] ^{4–} symmetric stretch	[P ₂ Se ₆] ^{4–} asymmetric stretches	[P ₂ Se ₆] ^{4–} bend	$[PSe_4]^{3-}$ or $[P_2Se_6]^{4-}$ bend
Raman shift (cm^{-1})	231 (s)	438 (s)	143 (w), 178 (w)	216 (s)	266 (s), 372 (w), 462 (w), 471 (w)	114 (w), 156 (s)	402 (w)

 $^{1}/_{\infty}[Sc_{2}(PSe_{4})_{2}(P_{2}Se_{6})^{4-}]$, which themselves organize in a crosshatched pattern. The compound showed no thermal transitions up to 600 °C, and the band gap was measured to be \sim 2.3 eV. Raman spectroscopy shows the symmetric and asymmetric stretches of the selenophosphate groups clearly, and they were assigned by analogy to known compounds. This system shows the versatility of the rare-earth-metal selenophosphate family because it forms another unique chain structure in an already varied library of interesting and complex compounds.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00535.

CIF of $K_4Sc_2P_4Se_{14}$ (CIF)

PXRD, SEM images, EDS analysis, atom crystallographic coordinates, and selected bond lengths (PDF)

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the National Science Foundation (Grant DMR- 1410169) and from the Nicholson Fellowship is gratefully acknowledged. The SEM/EDS work was performed in the EPIC facility of the NUANCE Center at Northwestern University. The NUANCE Center is supported by the NSF-DMR, Keck Foundation, State of Illinois, and Northwestern University.

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