Inorg. Chem. **2006**, *45*, 2785–2787

Inorganic Chemistry
Communication

$[P_6Se_{12}]^{4-}$: A Phosphorus-Rich Selenophosphate with Low-Valent P Centers

In Chung, Angela L. Karst, David P. Weliky, and Mercouri G. Kanatzidis*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received January 19, 2006

The new selenophosphate $Rb_4P_6Se_{12}$ features the *trans*-decalin-like, $[P_6Se_{12}]^{4-}$ anion, a phosphorus-rich species that possesses three parallel P–P bonds and formally P^{2+} and P^{4+} centers. The synthesis of $Rb_4P_6Se_{12}$ was accomplished with the reductive addition of P to $RbPSe_6$ and represents an interesting example of how alkali chalcophosphates can serve as starting materials to produce new compounds under mild reaction conditions.

The diversity found within the class of metal chalcophosphates is extensive.[1] Typically, these are ternary (M/P/Q) and quaternary (A/M/P/Q) compounds with $[P_xQ_y]^{z-}$ anions in their structure, where M is a metal, A is an alkali metal, and Q is sulfur or selenium. The selenophosphate anions that are structurally characterized include $[PSe_4]^{3-}$,[2] $[PSe_4]^{3-}\cdot 2Se_6$,[3] $[P_2Se_6]^{4-}$,[4] $[P_2Se_9]^{4-}$,[5] $[P_2Se_{10}]^{4-}$,[6] $[P_8Se_{18}]^{6-}$,[7] $[P_2Se_8]^{2-}$,[8] and the one-dimensional polymer $^1/_\infty[PSe_6^-]$.[9] All of these are P^{5+} species except for $[P_2Se_6]^{4-}$ and $[P_8Se_{18}]^{6-}$, which are formally P^{4+} and P^{4+}/P^{3+} compounds with P−P bonds, respectively. Each anion is capable of coordinating to a metal (M) and giving rise to extended structures.[1,10] Core questions in this chemistry include the limits of structural diversity and the stabilization of species with P in even lower oxidation states. Consequent phosphorus-rich phases have been rare in this chemistry. With this in mind, we conducted experiments aimed at stabilizing alkali salts of chalcophosphate anions by employing new synthetic conditions. In the present case, we attempted reductive reactions using $P^{5+}[P_xQ_y]^{z-}$ species as starting materials with an excess of elemental P. This chemistry was carried out at ∼400 °C with $RbPSe_6$ and red P and resulted in the new compound $Rb_4P_6Se_{12}$.

Here we describe the new polar chalcophosphate anion $[P_6Se_{12}]^{4-}$,[11] featuring P in two different oxidation states of 2+ and 4+. This is manifested in three parallel P−P bonds in the molecule. Direct combination reactions of Rb_2Se, P, and Se with the correct stoichiometric ratio could not produce this compound. The result suggests a unique suitability of alkali chalcophosphates as starting materials to explore new chemistry. This is partly due to their low melting points (300−400 °C) and high reactivity.

The new structure-type of $Rb_4P_6Se_{12}$[12] adopts the noncentrosymmetric space group $Pca2_1$. The compound features discrete $[P_6Se_{12}]^{4-}$ molecules (Figure 1a). The centrosymmetric molecule generates itself through a 2_1-screw axis along the *c* axis with no mirror plane perpendicular to the *c* axis and, consequently, crystallizes in a noncentrosymmetric fashion (Figure 1b). The most unusual feature of the structure is its bicyclic nature and the presence of three P−P bonds with two types of formal charges of P^{2+} and P^{4+}. The divalent formal charge is found on P2 and P5. The structure of the $[P_6Se_{12}]^{4-}$ molecule is reminiscent of the bicycloalkane *trans*-

---

* To whom correspondence should be addressed. E-mail: kanatzid@cem.msu.edu.

(1) Kanatzidis, M. G. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 139.

(2) Garin, J.; Parthe, E. *Acta Crystallogr.* **1972**, *B28*, 3672.

(3) Dickerson, C. A.; Fisher, M. J.; Sykora, R. E.; Albrecht-Schmitt, T. E.; Cody, J. A. *Inorg. Chem.* **2002**, *41*, 640.

(4) (a) Toffoli, P. P.; Khodadad, P.; Rodier, N. *Acta Crystallogr.* **1973**, *B34*, 1779. (b) Francisco, R. H. P.; Tepe, T.; Eckert, H. *J. Solid State Chem.* **1993**, *107*, 452.

(5) Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, *34*, 5401.

(6) Canlas, C. G.; Chung, I.; Kanatzidis, M. G.; Weliky, D. P. Manuscript in preparation.

(7) Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1998**, *37*, 2582.

(8) (a) Chung, I.; Kanatzidis, M. G. Manuscript in preparation. (b) Zhao, J.; Pennington, W. T.; Kolis, J. W. *J. Chem. Soc., Chem. Commun.* **1992**, 265.

(9) Chung, I.; Canlas, C. G.; Weliky, D. P.; Kanatzidis, M. G. *Inorg. Chem.* **2004**, *43*, 2762.

(10) (a) Do, J.; Yun, H. *Inorg. Chem.* **1996**, *35*, 3729. (b) Chen, J. H.; Dorhout, P. K.; Ostenson, J. E. *Inorg. Chem.* **1996**, *35*, 5627. (c) Gauthier, G.; Jobic, S.; Brec, R.; Rouxel, J. *Inorg. Chem.* **1998**, *37*, 2332. (d) Gieck, C.; Tremel, W. *Chem.*−*Eur. J.* **2002**, *8*, 2980.

(11) Pure $Rb_4P_6Se_{12}$ was achieved by a mixture of $RbPSe_6$:P = 1:4 under vacuum in a silica tube at 400 °C for 3 days, followed by washing with degassed *N*,*N*-dimethylformamide (DMF) under a N_2 atmosphere. Energy-dispersive spectroscopy microprobe analysis showed an average composition of "$Rb_{3.9}P_6Se_{11.7}$" for five orange irregular-shaped single crystals. The single crystals are stable in acetonitrile, DMF, and deionized water, and they are air-stable for over 1 week.

(12) Crystal data for $Rb_4P_6Se_{12}$ at 293(2) K: Siemens SMART Platform CCD diffractometer, Mo Kα radiation (λ = 0.710 73 Å), orthorhombic, $Pca2_1$, a = 16.409(3) Å, b = 10.640(2) Å, c = 15.105(3) Å, V = 2637.1(9) Å^3, Z = 4, D_c = 3.716 g/cm^3, μ = 24.296 mm^{-1}, 2θ = 1.91−28.29°, 22 687 total reflections, 6163 unique reflections with R(int) = 0.1274, refinement on F^2, GOF = 0.854, 199 parameters, R1 = 4.63%, wR2 = 7.69% for $I > 2\sigma(I)$, absolute structure parameter = 0.07(3). An empirical absorption correction was done using SADABS, and all atoms were refined anisotropically. Structure solution and refinement were performed using the SHELXTL package of crystallographic programs. The *PLATON* program (Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7) could not suggest additional symmetry, and the structure could not be solved in a centrosymmetric space group such as *Pbcm*.

10.1021/ic0601135 CCC: $33.50

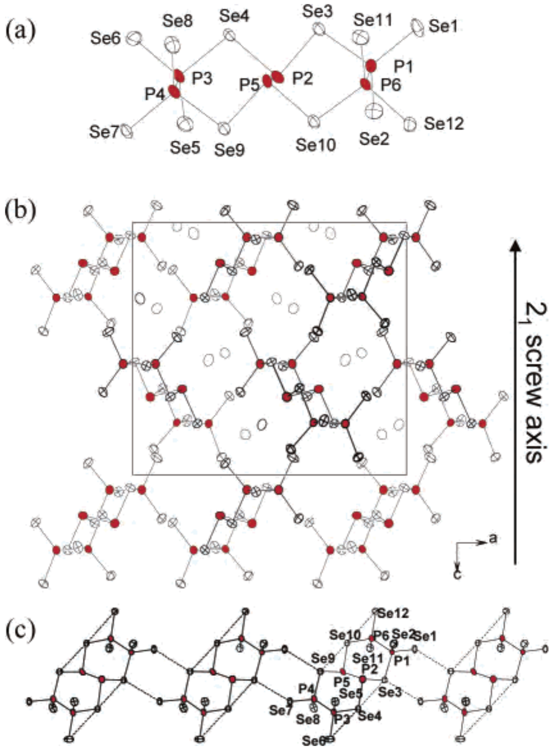

Figure 1. (a) $[P_6Se_{12}]^{4-}$ anion. (b) Structure of $Rb_4P_6Se_{12}$. (c) *Pseudo*-one-dimensional chain of $[P_6Se_{12}]^{4-}$ via Se⋯Se nonbonding contacts. Selected bond distances (Å): P1−Se1, 2.128(5); P1−Se2, 2.130(6); P1−Se3, 2.275(6); P2−Se3, 2.288(5); P2−Se4, 2.294(6); P3−Se4, 2.288(5); P3−Se5, 2.116(6); P3−Se6, 2.136(6); P4−Se7, 2.133(5); P4−Se8, 2.128(6); P4−Se9, 2.285(7); P5−Se9, 2.279(5); P5−Se10, 2.300(6); P6−Se10, 2.282(5); P6−Se11, 2.148(6); P6−Se12, 2.136(6); P1−P6, 2.241(7); P2−P5, 2.189(6); P3−P4, 2.257(7). Selected bond angles (deg): Se1−P1−Se2, 118.4(2); Se1−P1−Se3, 104.5(2); Se2−P1−Se3, 111.7(2); Se3−P2−Se4, 92.3(2); Se4−P3−Se5, 113.8(2); Se4−P3−Se6, 101.4(2); Se5−P3−Se6, 118.0(2); Se7−P4−Se8, 120.1(3); Se7−P4−Se9, 103.5(2); Se8−P4−Se9, 111.7(2); Se9−P5−Se10, 90.9(2); Se10−P6−Se11, 112.7(2); Se10−P6−Se12, 101.4(2); Se11−P6−Se12, 118.5(2); P1−P6−Se10, 104.7(2); P1−P6−Se11, 111.1(3); P1−P6−Se12, 107.2(3); P2−P5−Se9, 96.0(2); P2−P5−Se10, 96.7(2); P3−P4−Se7, 105.8(2); P3−P4−Se8, 111.6(3); P3−P4−Se9, 102.5(3); P4−P3−Se4, 103.0(2); P4−P3−Se5, 113.0(2); P4−P3−Se6, 105.9(3); P5−P2−Se3, 94.8(2); P5−P2−Se4, 96.7(2); P6−P1−Se1, 104.7(2); P6−P1−Se2, 112.8(3); P6−P1−Se3, 103.2(2). Dashed lines indicate weak Se⋯Se nonbonding interactions (Å): Se1⋯Se9, 3.384(3); Se3⋯Se4, 3.273(3); Se3⋯Se7, 3.340(3); Se4⋯Se6, 3.413(3); Se9⋯Se10, 3.276(3); Se10⋯Se12, 3.416. The thermal ellipsoids are shown with 50% probability.

decalin. The central P_2 unit is condensed with two ethane-like $[P_2Se_6]^{4-}$ fragments to form the decalin-like skeleton.

The $[P_6Se_{12}]^{4-}$ molecule adopts the C_{2h} point group, so that the central $[P_2Se_4]$ subunit has a *trans*-C_{2h}-type configuration around the P^{2+} centers. The same *trans*-C_{2h}-type configuration is found in P_2X_4 (X = F, Cl, I).[13] The Se−P−Se angles around P2 and P5 are nearly 90° [Se3−P2−Se4, 92.3(2)°; Se9−P5−Se10, 90.9(2)°]. The dihedral angles of Se3−P2−P5−Se9 and Se4−P2−P5−Se10 are 178.76(20) and −179.74(20)°, respectively. As a result, the P2−P5 vector defines the intersection of two planes. The outer $[P_2Se_6]$ residues in the molecule represent typical anti-type conformations but are distorted. (See relevant angles in the caption of Figure 1.) The P−Se distances are normal at 2.116(6)−2.300(6) Å. The Se−P−Se angles range from 90.9(2) to 120.1(3)°. The P2−P5 distance is 2.189(6) Å, which is only slightly shorter than the typical P−P distance of ∼2.2 Å in selenophosphates. Rhombohedral black P shows a P−P distance of 2.13 Å.[14]

To the best of our knowledge, this is a unique anion. The only other anion with formally P^{2+} centers is the polymeric $^{1}/_{\infty}[P_5Se_{10}{}^{5-}]$, which is strongly bound to transition-metal atoms in $A_3MP_5Se_{10}$ (A = K, Rb; M = Ru, Os).[15,16] In these compounds, the P^{2+} centers are coordinated to Ru^{2+} or Os^{2+} metal centers through the P atoms, forming P−M bonds (M = Ru, Os).

Interestingly, the atoms Se1⋯Se3⋯Se4⋯Se6 are collinear, which allows maximum overlap of their pπ orbitals. The Se7⋯Se9⋯Se10⋯Se12 atoms are similarly collinear. The intramolecular Se3⋯Se4, Se4⋯Se6, Se9⋯Se10, and Se10⋯Se12 distances range from 3.273(3) to 3.416(3) Å and indicate both nonbonding interactions and severely distorted Se−P−Se angles in the central $[P_2Se_4]$ subunit. Similar intramolecular interactions have been observed in the $[PSe_3]$ pyramidal fragment of the $[P_8Se_{18}]^{6,7}$ anion and the $^{1}/_{\infty}[PSe_6{}^{-}]$ chain in $CsPSe_6$.[9]

Another notable feature is the unusually short intermolecular Se1⋯Se9 and Se3⋯Se7 distances of 3.384(3) and 3.340(3) Å, respectively. These distances indicate nonbonding interactions, but they are much shorter than the 3.80 Å sum of the van der Waals radii.[17] They enable the molecules of $[P_6Se_{12}]^{4-}$ to organize to an infinite *pseudo*-one-dimensional structure (Figure 1c). Low-dimensional compounds such as $NbSe_3$[18] and $APSe_6$ (A = K, Rb, Cs) display similar Se⋯Se interactions. These intermolecular interactions may contribute to the compound's stability in air and polar solvents such as water and *N*,*N*-dimethylformamide.

The synthesis of $Rb_4P_6Se_{12}$ adds further insight in the close relationship between the structure and the flux condition (or A:P:Se ratio) in the alkali selenophosphate ternary system. More basic fluxes (i.e., those with a high A:P ratio) or higher reaction temperatures tend to give shorter structural fragments[19] and P in the 5+ oxidation state (Table 1). All simple anions, e.g., $[PSe_4]^{3-}$ and $[P_2Se_9]^{4-}$, were prepared in strongly basic fluxes (Table 1). As the basicity decreases, more complex species emerge, such as $[P_2Se_6]^{4-}$, $[P_8Se_{18}]^{4-}$, and $[P_2Se_8]^{2-}$. Under even less basic flux conditions, the one-dimensional polyselenide chain $^{1}/_{\infty}[PSe_6{}^{-}]$ is stabilized with K, Rb, and Cs. $Rb_4P_6Se_{12}$ is made in intermediate acidic/basic conditions, and it contains P^{2+} centers because of excess P.

Differential thermal analysis (DTA) on $Rb_4P_6Se_{12}$ at a rate of 10 °C/min showed melting at ∼431 °C and crystallization

---

(13) Corbridge, D. E. C. *Phosphorus, An Outline of its Chemistry, Biochemistry and Uses*, 5th ed.; Elsevier: New York, 1995; p 143.

(14) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: New York, 1974; p 16.

(15) Chondroudis, K.; Kanatzidis, M. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1324.

(16) Chung, I.; Kanatzidis, M. G. Unpublished results.

(17) Shannon, R. D. *Acta Crystallogr*. **1964**, *A32*, 751.

(18) (a) *Electronic Properties of Inorganic Quasi-One-Dimensional Compounds*; Monceau, P., Ed.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1985; Part II. (b) Canadell, E.; Rachidi, E.-I.; Pouget, J. P.; Gressier, P.; Meerschaut, A.; Rouxel, J.; Jung, D.; Evain, M.; Whangbo, M.-H. *Inorg. Chem*. **1990**, *29*, 1401.

(19) Kanatzidis, M. G.; Sutorik, A. *Prog. Inorg. Chem.* **1995**, *43*, 151.

Table 1. Relationship between Observed Selenophosphate Species and the A:P:Se Ratio[a]

known compounds	anion	A:P:Se ratio[b]	flux condition	note
A_3PSe_4 (A = Na, K, Cs[16])	$[PSe_4]^{3-}$	3:1:4	basic	discrete molecular
$Cs_4P_2Se_{10}$	$[P_2Se_{10}]^{4-}$	2:1:5		
$A_4P_2Se_9$ (A = K, Rb, Cs)	$[P_2Se_9]^{4-}$	2:1:4.5		
$A_4P_2Se_6$ (A = Na, K[16])	$[P_2Se_6]^{4-}$	2:1:3		
$A_6P_8Se_{18}$ (A = K,[7] Rb, Cs[16])	$[P_8Se_{18}]^{6-}$	1:1.33:3	intermediate	
$Rb_4P_6Se_{12}$	$[P_6Se_{12}]^{4-}$	1:5:6		double six-membered ring
$Cs_2P_2Se_8$	$[P_2Se_8]^{2-}$	1:1:4	"acidic"	six-membered ring
$K_2P_2Se_6$	$^{1}_{\infty}[P_2Se_6{}^{2-}]$	1:1:3		one-dimensional chain
$APSe_6$ (A = K, Rb, Cs)	$^{1}_{\infty}[PSe_6{}^{-}]$	1:1:6		

[a] All compounds have been structurally refined by single-crystal X-ray diffraction. [b] These are typical ratios. In fact, there are ranges in these ratios that define a given flux condition and can lead to the compounds shown.

upon cooling at ~384 °C. X-ray diffraction patterns for samples before and after DTA were identical. The results suggest that $Rb_4P_6Se_{12}$ could be a promising precursor in synthesis for further reaction chemistry. The UV−vis spectrum reveals a sharp absorption edge and a band gap of 2.25 eV, which is in good agreement with its orange color. By comparison, the one-dimensional $RbPSe_6$ with P^{5+} showed a gap of 2.18 eV. The Raman spectrum of $Rb_4P_6Se_{12}$ shows shifts at 218 (vs), 298 (vw), 348(w), 371 (w), 414 (w), 487 (w), and 516 (vw) cm^{-1}. The peak at 218 cm^{-1} is unambiguously assigned to the locally A_{1g} symmetric stretching mode of PSe_3.[20] The second shift at 298 cm^{-1} resembles the ν_{12} (B_g) mode in $Pb_2P_2Se_6$ having C_{2h} site symmetry.[21] The other vibrations can be attributed to PSe_3 stretching modes.[4,22] The far-IR spectrum is rather complex, showing peaks at 214 (vs), 238 (bw), 301 (vw), 319 (vw), 353 (vw), 374 (vw), 392 (vw), 408 (w), 464 (vw), 486 (vw), 514 (w), and 524 (w) cm^{-1}. The peak at 319 cm^{-1} is assigned to a P−P vibration and was not observed in the Raman spectrum. Other peaks are well matched with those of $Pb_2P_2Se_6$ and other compounds that contain the $[P_2Se_6]^{4-}$ anion.[23]

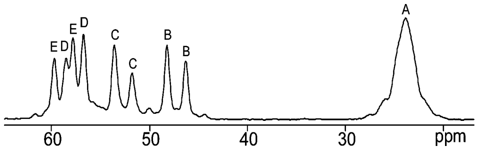

Figure 2. Bloch decay ^{31}P NMR spectrum of $Rb_4P_6Se_{12}$ taken at ambient temperature on a 9.4-T spectrometer. Acquisition parameters included a 5-μs $\pi/2$ pulse, a 8000-s relaxation delay, and a 13-kHz magic-angle-spinning frequency. The chemical shift reference was 85% H_3PO_4 (0 ppm). Peaks with the same letter are *J*-coupled. The average chemical shifts of peaks A−E are in the order 23.9, 47.5, 52.6, 57.6, and 58.8 ppm. The *J* couplings of doublets B−E are 309, 292, 295, and 309 Hz.

Figure 2 displays the ^{31}P NMR spectrum of $Rb_4P_6Se_{12}$. The narrow line widths afford resolution of most of the P sites. The ratio of the integrated intensity of the B−E cluster of peaks to the intensity of peak A is ~2 and is generally consistent with the assignment of P1, P3, P4, and P6 to the B−E peaks and P2 and P5 to the A peak. P1/P6 and P3/P4 *J* couplings are expected, and analysis of the spectrum yielded the same *J* coupling for doublets B and E and the same *J* coupling for doublets C and D. The isotropic chemical shifts and *J* couplings were confirmed by the analysis of spectra taken on a 7-T spectrometer. It was not possible to make a more detailed assignment of P1/P6 and P3/P4 to the C/D and B/E doublets, and the P2/P5 shifts were not resolved from one another. The ^{31}P NMR chemical shifts are all >0 ppm and are consistent with the positive chemical shifts of other metal selenophosphates with P−P bonding.[24]

The discovery of the molecular salt $Rb_4P_6Se_{12}$ with its unique bicycloselenophosphate anion and rare combination of P^{2+} and P^{4+} centers suggests a more extensive compositional diversity in alkali chalcophosphates. The unraveling relationship between basicity and the final structure enhances the understanding of flux chemistry and the prospects of the future discovery of new materials in this class of solids.

Acknowledgment. Financial support was provided by the National Science Foundation (Grant DMR-0443783). We thank Erin Wimmers for NMR assistance.

Supporting Information Available: X-ray crystallographic file (in CIF format) as well as UV−vis, FTIR, and Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0601135

---

(20) Mathey, Y.; Clement, R.; Sourisseau, C.; Lucazeau, G. *Inorg. Chem.* **1980**, *19*, 2773.

(21) Becker, R.; Brockner, W. *Z. Naturforsch.* **1984**, *39a*, 357.

(22) Chondroudis, K.; Charkrabarty, D.; Axtell, E. A.; Kanatzidis, M. G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 975.

(23) Parensen, M.; Brockner, W.; Cyvin, B. N.; Cyvin, S. J. *Z. Naturforsch.* **1986**, *41a*, 1233.

(24) Canlas, C. G.; Kanatzidis, M. G.; Weliky, D. P. *Inorg. Chem.* **2003**, *42*, 3399.