

[P₃Se₇]³⁻: A Phosphorus-Rich Square-Ring Selenophosphate

In Chung,[†] Daniel Holmes,[‡] David P. Weliky,[‡] and Mercouri G. Kanatzidis^{*†}

[†]Department of Chemistry, Northwestern University, Evanston, Illinois 60208, and [‡]Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received January 13, 2010

The new compound Cs₁₀P₈Se₂₀ features the heterotetracyclic [P₃Se₇]³⁻ anion, a phosphorus-rich four-membered-ring species that possesses a P–P–P unit and formally P³⁺ and P⁴⁺ centers. It crystallizes in the orthorhombic space group *Pnnm* with *a* = 26.5456(7) Å, *b* = 8.0254(2) Å, *c* = 11.9031(4) Å, and *Z* = 2 at 100(2) K. The cyclic anion is cocrystallized with a [P₂Se₆]⁴⁻ anion. Electronic absorption, Raman, Fourier transform infrared, and solid-state ³¹P NMR spectroscopy studies of Cs₁₀P₈Se₂₀ are reported.

Chalcophosphates are typically ternary (A/P/Q and M/P/Q) and quaternary (A/M/P/Q) compounds with [P_{*x*}Se_{*y*}]^{*n-*} anions in their structure, where M is a metal, A is an alkali metal, and Q is sulfur or selenium. The broad diversity of this class of compounds is attributed to various binding modes and reactivities of chalcophosphate anions in salt fluxes to coordinating metals.¹ Indeed, many selenophosphate ligands have been structurally characterized, for example, [P₂Se₈]²⁻,² [P₂Se₉]⁴⁻,³ [P₂Se₁₀]⁴⁻,⁴ [PSe₄]³⁻,⁵ 2Se₆,⁵ [P₈Se₁₈]⁶⁻,⁶ [PSe₆]⁻,⁷ [P₂Se₆]²⁻,⁸

α-[P₆Se₁₂]⁴⁻,⁹ β-[P₆Se₁₂]⁴⁻, and [P₅Se₁₂]⁵⁻.¹⁰ The common oxidation states of phosphorus in selenophosphates are P⁴⁺ and P⁵⁺. Because members of this family can exhibit technologically important ferroelectric,¹¹ nonlinear optical,^{8,10,12} reversible redox chemistry relevant to secondary batteries,¹³ photoluminescence,¹⁴ and phase-change properties,¹⁵ it is important to understand the limits of structural diversity beyond the simple [PSe₄]³⁻ and [P₂Se₆]⁴⁻ anions and how to stabilize the desirable species.

Our previous investigations of chalcophosphate compounds provided new insights into the relationship between the structure and flux composition (i.e., A:P:Se ratio).⁹ We also found that excess phosphorus in the flux helps to produce less oxidized P^{2+/3+/4+} species such as A₆P₈Se₁₈ (A = K, Rb, Cs),⁶ A₄P₆Se₁₂ (A = Rb,⁹ Cs), and Cs₅P₅Se₁₂.¹⁰ In fact, except for metal phosphides,¹⁶ compounds containing phosphorus in low formal oxidation states are largely limited to organic or organometallic species¹⁷ such as transient phosphinidenes and their derivatives, catenated polyphosphines, and elemental P.¹⁶

Here we describe the novel heterocyclic anion of [P₃Se₇]³⁻ found in the new compound Cs₁₀P₈Se₂₀.¹⁸ The cyclic anion features a ring structure and phosphorus in two different formal oxidation states, 3+ and 4+. The ring seems highly strained with a rare P–P–P unit (∠P(2)–P(1)–P(2) ~ 90°). The [P₃Se₇]³⁻ molecule cocrystallizes with the ethane-like [P₂Se₆]⁴⁻ anion to form Cs₁₀P₈Se₂₀. [P_{*x*}Se_{*y*}]^{*n-*} anions with a ring structure are uncommon, and only a few have been structurally characterized, i.e., [P₂Se₈]²⁻,² α,β-[P₆Se₁₂]⁴⁻,⁹ and [P₅Se₁₂]⁵⁻.¹⁰

*To whom correspondence should be addressed. E-mail: m-kanatzidis@northwestern.edu.

- (1) Kanatzidis, M. G. *Curr. Opin. Solid State Mater. Sci.* **1997**, 2, 139.
- (2) (a) Chung, I.; Kanatzidis, M. G. Cs₂P₂Se₈: Unpublished results. (b) Zhao, J.; Pennington, W. T.; Kolis, J. W. *J. Chem. Soc., Chem. Commun.* **1992**, 265. (c) Rotter, C.; Schuster, M.; Kidik, M.; Schon, O.; Klapotke, T. M.; Karaghiosoff, K. *Inorg. Chem.* **2008**, 47, 1663.
- (3) Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, 34, 5401.
- (4) Gave, M. A.; Canlas, C. G.; Chung, I.; Iyer, R. G.; Kanatzidis, M. G.; Weliky, D. P. *J. Solid State Chem.* **2007**, 180, 2877.
- (5) Dickerson, C. A.; Fisher, M. J.; Sykora, R. E.; Albrecht-Schmitt, T. E.; Cody, J. A. *Inorg. Chem.* **2002**, 41, 640.
- (6) Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1998**, 37, 2582.
- (7) Chung, I.; Do, J.; Canlas, C. G.; Weliky, D. P.; Kanatzidis, M. G. *Inorg. Chem.* **2004**, 43, 2762.
- (8) Chung, I.; Malliakas, C. D.; Jang, J. I.; Canlas, C. G.; Weliky, D. P.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2007**, 129, 14996.
- (9) Chung, I.; Karst, A. L.; Weliky, D. P.; Kanatzidis, M. G. *Inorg. Chem.* **2006**, 45, 2785.
- (10) Chung, I.; Jang, J. I.; Gave, M. A.; Weliky, D. P.; Kanatzidis, M. G. *Chem. Commun.* **2007**, 4998.
- (11) (a) Carpentier, C. D.; Nitsche, R. *Mater. Res. Bull.* **1974**, 9, 1097. (b) Scott, B.; Pressprich, M.; Willet, R. D.; Cleary, D. A. *J. Solid State Chem.* **1992**, 96, 294.
- (12) (a) Chung, I.; Jang, J. I.; Malliakas, C. D.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2010**, 132, 384. (b) Chung, I.; Song, J. H.; Jang, J. I.; Freeman, A. J.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2009**, 131, 2647. (c) Lacroix, P. G.; Clement, R.; Nakatani, K.; Zyss, J.; Ledoux, I. *Science* **1994**, 263, 658.

- (13) Lemehaute, A.; Ouvrard, G.; Brec, R.; Rouxel, J. *Mater. Res. Bull.* **1977**, 12, 1191.
- (14) Huang, Z. L.; Cajipe, V. B.; Lerolland, B.; Colombet, P.; Schipper, W. J.; Blasse, G. *Eur. J. Solid State Inorg. Chem.* **1992**, 29, 1133.
- (15) (a) Breshears, J. D.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2000**, 122, 7839. (b) McCarthy, T. J.; Kanatzidis, M. G. *Chem. Mater.* **1993**, 5, 1061. (c) McCarthy, T. J.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, 34, 1257. (d) Kanatzidis, M. G.; Huang, S. P. *Inorg. Chem.* **1989**, 28, 4667.
- (16) von Schnering, H. G.; Hönl, W. *Chem. Rev.* **1988**, 88, 243–273.
- (17) Ellis, B. D.; Macdonald, C. L. B. *Inorg. Chem.* **2006**, 45, 6864–6874.
- (18) The synthesis of Cs₁₀P₈Se₂₀ was achieved by reacting the 1:2:2 Cs₂Se₂/P/Se mixture under vacuum in a fused-silica tube at 600 °C for 3 days followed by cooling to 250 °C at a rate of 5 °C h⁻¹ and room temperature in 3 h. The products were washed with degassed *N,N*-dimethylformamide, acetonitrile, and ether under a N₂ atmosphere to reveal pure orange crystals of Cs₁₀P₈Se₂₀. The yield was ~70% based on phosphorus. The crystals are stable in alcohol, water, and air and are slightly soluble in *N*-methylformamide.

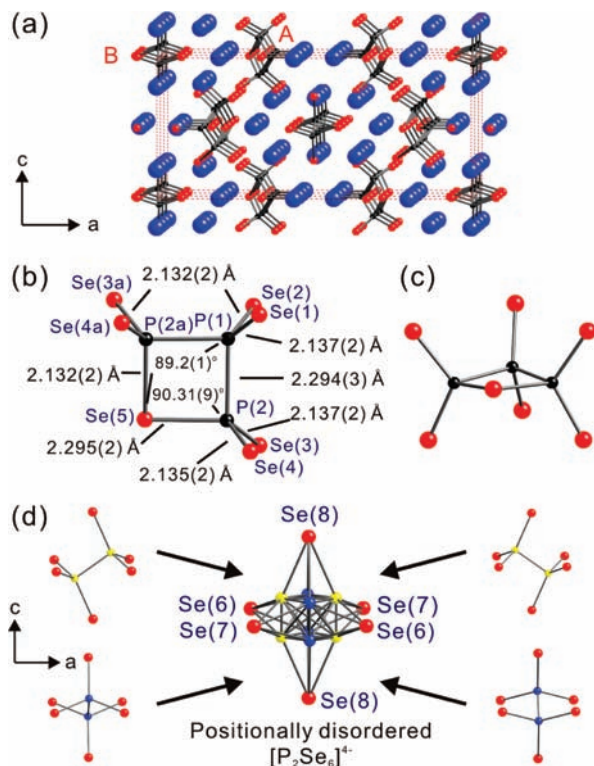
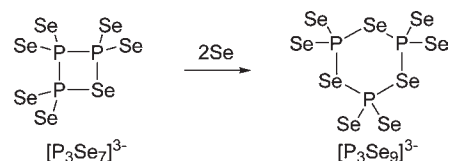


Figure 1. (a) Structure of $\text{Cs}_{10}\text{P}_8\text{Se}_{20}$ viewed down the b axis. The $[\text{P}_3\text{Se}_7]^{3-}$ anion is labeled as “A” and the $[\text{P}_2\text{Se}_6]^{4-}$ anion as “B”. Color code: blue, Cs atoms; black, P atoms; red, Se atoms. (b and c) Structure of the $[\text{P}_3\text{Se}_7]^{3-}$ square anion. P and Se atoms are labeled. Bond distances (Å) and angles (deg) are represented. Symmetrically equivalent atoms are denoted as “a”. (d) Example of an apparently complex, disordered $[\text{P}_2\text{Se}_6]^{4-}$ anion sitting on $(0, 0.5, z)$, one of the special positions of the $Pnmm$ space group. It is a superimposed image of four $[\text{P}_2\text{Se}_6]^{4-}$ units in different orientations that share the same center of symmetry at the special position. Color code: blue, P(3) atoms; yellow, P(4) atoms; red, Se atoms. Each Se atom is labeled.

The new structure type of $\text{Cs}_{10}\text{P}_8\text{Se}_{20}$ crystallizes in the $Pnmm$ space group.¹⁹ The compound is best described as a double salt $[\text{Cs}_3[\text{P}_3\text{Se}_7]_2] \cdot [\text{Cs}_4[\text{P}_2\text{Se}_6]]$ and contains two discrete molecules of $[\text{P}_3\text{Se}_7]^{3-}$ (A) and one of $[\text{P}_2\text{Se}_6]^{4-}$ (B) (Figure 1a). The $[\text{P}_3\text{Se}_7]^{3-}$ anion is structurally unique, and its most unusual feature is the heterocyclic square composed of one Se atom and three P atoms. A P–P–P unit with two types of the formal charges of P^{3+} and P^{4+} are found on the ring (Figure 1b). The trivalent formal charge is found on P(1). A mirror plane bisects the noncentrosymmetric molecule to give the C_m point group, with P(2) being related with P(2a) by the reflection symmetry operation. The nearly square-planar $[\text{P}_3\text{Se}_7]^{3-}$ is slightly folded parallel to the mirror plane to form a kite shape (Figure 1b,c): $\angle \text{P}(2)–\text{P}(1)–\text{P}(2)$, $89.2(1)^\circ$; torsion angle of $\text{P}(1)–\text{P}(2)–\text{Se}(5)–\text{P}(2)$, 7.468° . Note that the $\text{P}(2)–\text{Se}(5)$ distance, $2.295(2)$ Å, is very close to that of $\text{P}(1)–\text{P}(2)$ at $2.294(3)$ Å. The $\text{P}(1)–\text{P}(2)$ distance is significantly longer than those normally found in other chalcophosphate compounds ($2.18–2.22$ Å), implying the existence of strain in the four-membered ring. The strain implies a possible reactive tendency of this anion toward

Scheme 1



relieving it. For example, we expect the addition of 2 equiv of Se to $[\text{P}_3\text{Se}_7]^{3-}$ to result in the new inorganic ring species of $[\text{P}_3\text{Se}_9]^{3-}$ according to Scheme 1.

Compounds with homocyclic P_4 units have been structurally characterized, e.g., $(\text{NH}_4)_4[\text{P}_4\text{S}_8] \cdot 2\text{H}_2\text{O}$ ²⁰ and $\text{Cs}_2\text{P}_4 \cdot 2\text{NH}_3$,²¹ and similarly long P–P distances were also observed in $[\text{P}_4\text{S}_8]^{4-}$ at $2.280(1)$ and $2.287(1)$ Å, which consists of four tetraordinated P atoms with two terminal S atoms on each P atom.²⁰ The Se analogue to this molecule is not yet reported. Even longer P–P bond distances were found in neutral cage-like phosphorus sulfides such as P_4S_7 at $2.326(7)$ Å²² and $\alpha\text{-P}_4\text{S}_4$ at $2.360(3)$ Å.²³ Because of the four-membered ring structure of the $[\text{P}_3\text{Se}_7]^{3-}$ anion, unusually short, nonbonding intramolecular interactions are observed for $\text{P}(2) \cdots \text{P}(2a)$ at $3.222(3)$ Å, $\text{P}(1) \cdots \text{Se}(4)$ at $3.647(2)$ Å, $\text{P}(1) \cdots \text{Se}(5)$ at $3.254(3)$ Å, and $\text{Se}(3) \cdots \text{Se}(5)$ at $3.645(1)$ Å. These distances are shorter than the sum of the ionic radii of atoms.²⁴

The seemingly complex, discrete anion B is a superimposed image of four positionally disordered, ethane-like $[\text{P}_2\text{Se}_6]^{4-}$ anions (Figure 1d). The site occupancy of P(3) and P(4) atoms is 25%, respectively. The $[\text{P}_2\text{Se}_6]^{4-}$ anions disorder because they reside on the fixed-symmetry elements that they do not possess, i.e., on the special positions of the $Pnmm$ space group: $(0, 0.5, z)$, Wyckoff position 4f, site symmetry 2; $(0.5, 0, 0.5)$, Wyckoff position 2c, site symmetry $2/m$. The $[\text{P}_2\text{Se}_6]^{4-}$ molecule adopts the D_{3h} point group when ideal, and the P–P bonds of the anions are tilted with respect to the crystallographic c axis. Because the atomic sites in the unit cell are defined by symmetry elements, the $[\text{P}_2\text{Se}_6]^{4-}$ anions that do not satisfy such site symmetries, 2 and $2/m$, are forced to be positionally disordered. Because all Se atom positions are arranged octahedrally, they are superimposed for all orientations of the X anion. Thus, the Se atoms appear ordered, and it is only the P–P bonds that change direction. A similar symmetry-related disorder is found in $[\text{Mo}_2\text{Cl}_8]^{2-}$.²⁵

The synthesis of $\text{Cs}_{10}\text{P}_8\text{Se}_{20}$ provides further insight into the close relationship between the structure and flux condition (or A:P:Se ratio) and how the low-valent P species in the alkali selenophosphate class can be stabilized. The remarkably rich structural chemistry of the Cs/P/Se system is summarized in Table 1. More basic fluxes (i.e., those with a high A:P ratio) or higher reaction temperatures tend to give shorter structural fragments²⁶ and phosphorus in the 5+ oxidation state. As the basicity decreases, more complex species emerge such as the one-dimensional polyselenide chains $[\text{PSe}_6]^-$ and $[\text{P}_2\text{Se}_6]^{2-}$.

(20) Falius, H.; Krause, W.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 103.

(21) Kraus, F.; Korber, N. *Chem.—Eur. J.* **2005**, *11*, 5945.

(22) Vos, A.; Olthof, R.; Vanbolhu, F.; Botterwe, R. *Acta Crystallogr.* **1965**, *19*, 864.

(23) Griffin, A. M.; Minshall, P. C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1976**, 809.

(24) Shannon, R. D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1976**, *32*, 751.

(25) Cotton, F. A.; Eglin, J. L. *Inorg. Chim. Acta* **1992**, *198–200*, 13.

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

(19) Crystal data for $\text{Cs}_{10}\text{P}_8\text{Se}_{20}$ at $100(2)$ K: STOE IPDS 2T diffractometer, $\text{Mo K}\alpha$ radiation at $(\lambda = 0.71073 \text{ Å})$, orthorhombic, $Pnmm$, $a = 26.5456(7) \text{ Å}$, $b = 8.0254(2) \text{ Å}$, $c = 11.9031(4) \text{ Å}$, $V = 2535.8(1) \text{ Å}^3$, $Z = 2$, $D_c = 4.133 \text{ g cm}^{-3}$, $\mu = 21.771 \text{ mm}^{-1}$, $2\theta = 3.06–50.52^\circ$, 15751 total reflections, 2242 unique reflections with $R_{\text{int}} = 5.55\%$, $\text{GOF} = 1.159$, 118 parameters, $R1 = 3.39\%$, $wR2 = 7.79\%$ for $I > 2\sigma(I)$.

Table 1. Complex Structural Chemistry of the Cs/P/Se System: Relationship between the Observed Selenophosphate Species and the A:P:Se Ratio in the Flux^a

compound	A:P:Se ratio ^b	anion	flux condition	color	note
Cs ₃ PSe ₄ ²⁷	3:1:4	[PSe ₄] ³⁻	basic	yellow	discrete molecule
Cs ₇ P ₃ Se ₁₃ ^c	2.33:1:4.33	[P ₂ Se ₉] ⁴⁻ · [PSe ₄] ³⁻		red	discrete molecule
Cs ₄ P ₂ Se ₁₀ ⁴	2:1:5	[P ₂ Se ₁₀] ⁴⁻		red	discrete molecule
Cs ₄ P ₂ Se ₉ ³	2:1:4	[P ₂ Se ₉] ⁴⁻		red	discrete molecule
Cs ₁₀ P ₈ Se ₂₀	1.25:1:2.5	2[P ₃ Se ₇] ³⁻ · [P ₂ Se ₆] ⁴⁻	intermediate	orange	ring included
Cs ₄ P ₄ Se ₁₄ ^c	1:1:3.5	[P ₂ Se ₆] ²⁻ · [P ₂ Se ₈] ²⁻		red	two-ring molecules
Cs ₄ P ₆ Se ₁₂ ¹⁰	1:1.5:3	β-[P ₆ Se ₁₂] ⁴⁻		orange	ring, PC ^d
Cs ₅ P ₅ Se ₁₂ ¹⁰	1:1:2.4	[P ₅ Se ₁₂] ⁵⁻		red	ring, PC, SHG ^e
Cs ₆ P ₈ Se ₁₈ ⁶	1:1.33:3	[P ₈ Se ₁₈] ⁶⁻		red	oligomer
"Cs ₃ P ₃ Se ₇ " ^f	1:1:2.33	[P ₃ Se ₇] ³⁻			ring
Cs ₂ P ₂ Se ₈ ^{2a}	1:1:4	[P ₂ Se ₈] ²⁻	"acidic"	orange	ring
Cs ₂ P ₂ Se ₆	1:1:3	¹ ₂ [P ₂ Se ₆] ²⁻		orange	1-D, PC, SHG
CsPSe ₆ ⁷	1:1:6	[∞] ₁ [PSe ₆] ⁻		orange	1-D, PC

^a All compounds have been structurally refined by single-crystal 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. ^c Unpublished results. ^d Crystal-glass phase-change (PC) behavior shown.

^e Nonlinear optical second-harmonic generation (SHG) response observed. ^f "Cs₃P₃Se₇" in Cs₁₀P₈Se₂₀ was represented for comparison with other cyclic selenophosphate anions.

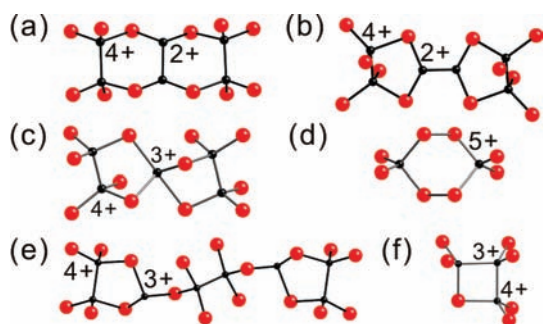


Figure 2. Examples of the selenophosphate anions isolated from intermediate/less basic flux conditions: (a) α-[P₆Se₁₂]⁴⁻; (b) β-[P₆Se₁₂]⁴⁻; (c) [P₅Se₁₂]⁵⁻; (d) [P₂Se₈]²⁻; (e) [P₈Se₁₈]⁶⁻; (f) [P₃Se₇]³⁻. The formal charge on P centers is represented.

In this work, we examined the intermediate "acidic"/basic conditions with an excess of phosphorus. If we count "Cs₃P₃Se₇" in Cs₁₀P₈Se₂₀ as an independent species, all species in those A:P:Se ranges, i.e., [P₈Se₁₈]⁶⁻, [P₆Se₁₂]⁴⁻, [P₅Se₁₂]⁵⁻, and [P₃Se₇]³⁻, possess the less oxidized P^{2+/3+/4+} with mixed formal charge centers on P and adopt a ring-type molecular structure (Figure 2).

We could only obtain Cs₁₀P₈Se₂₀ by a flux reaction. Our attempts to synthesize the single salt "Cs₃[P₃Se₇]" by a direct combination reaction gave only Cs₅P₅Se₁₂,¹⁰ which is not surprising because it is compositionally very close to Cs₃P₃Se₇, i.e., with the Cs:P:Se ratio being 1:1:2.33 for the former and 1:1:2.4 for the latter. A total of 1 mol of excess P (Cs₂Se₂:P:Se = 1:3:2) to the flux condition of the title compound produced a red glass.

According to differential thermal analysis performed at a rate of 10 °C min⁻¹, Cs₁₀P₈Se₂₀ melts incongruently at ~392 °C and the melt crystallizes at ~364 °C. The powder X-ray diffraction pattern after recrystallization indicated Cs₁₀P₈Se₂₀ and a small amount of orange glass. The solid-state optical absorption spectrum revealed a well-defined absorption edge at 2.07 eV, consistent with its orange color (Figure S1 in the Supporting Information). By comparison, the ring-type compounds Cs₅P₅Se₁₂ with P^{3+/4+} and Cs₄P₆Se₁₂ with P^{2+/4+} showed a band gap at 2.17 eV.

Solid-state ³¹P magic angle spinning (MAS) NMR spectroscopy of polycrystalline samples of Cs₁₀P₈Se₂₀ gave three sets of isotropic peaks at 52.5 ppm, (64.5 + 66.0) ppm, and (94.6 + 95.9) ppm (Figure 3). These peaks were identified by a

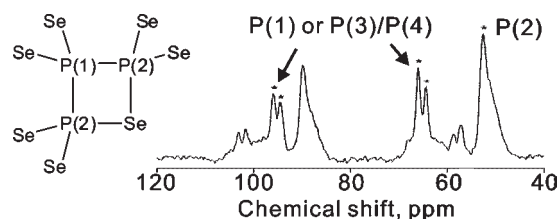


Figure 3. Solid-state ³¹P MAS NMR spectrum of polycrystalline Cs₁₀P₈Se₂₀ at a 9.4 T field and a 6.0 kHz spinning frequency with the dominant isotropic peaks highlighted by asterisks. The [P₃Se₇]³⁻ anion is represented.

comparison of spectra at different spinning frequencies, and the remaining peaks can be assigned as spinning sidebands. Considering both isotropic and spinning sideband peaks, the overall integrated intensities for the 52.5 ppm, (64.5 + 66.0) ppm, and (94.6 + 95.9) ppm peaks were ~2:1:1, which suggests an assignment of the 52.5 ppm peak to P(2), the (64.5 + 66.0) ppm peak to P(1) or P(3)/P(4), and the (94.6 + 95.9) ppm peak to the remaining P. The result supports the crystal structure of Cs₁₀P₈Se₂₀, which indicates three magnetically independent P atoms [P(3) and P(4) are locally and magnetically identical]. The positive isotropic shifts and overall separation of ~150 ppm between extreme splitting sidebands of peaks are consistent with P–P bonding in this compound.²⁸

The molecular salt Cs₁₀P₈Se₂₀ stabilizes the new inorganic heterotetracyclic anion with its low-oxidation-state P³⁺ and P⁴⁺ centers and highly strained intraring bonds. Its discovery highlights the rich chemical diversity of the [P_nSe_n]ⁿ⁻ system and the importance of the relationship between the basicity and final products.

Acknowledgment. Financial support was provided by the National Science Foundation (Grant DMR-0801855).

Supporting Information Available: X-ray crystallographic file (in CIF format), experimental details, crystallographic refinement data, and optical absorption, FT-IR, Raman, and NMR spectroscopy data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(27) Knaust, J. M.; Dorhout, P. K. *J. Chem. Crystallogr.* **2006**, *36*, 217.

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