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$[P_8Se_{18}]^{6-}$: A New Oligomeric Selenophosphate Anion with P^{4+} and P^{3+} Centers and Pyramidal $[PSe_3]$ Fragments

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Introduction

The application of polychalcophosphate fluxes for the synthesis of new chalcophosphates has made substantial contributions in the development of this class of compounds.[1−4] The in situ fusion of $A_2Q/P_2Q_5/Q$ (A = alkali metal; Q = S, Se) forms highly reactive $[P_yQ_z]^{n-}$ anions solubilized in an excess of polychalcogenide flux. These species, in the presence of metal ions, coordinate and become the building blocks of new polymeric or molecular structures. The isolation and identification of such anions will help us understand better the nature of these fluxes and provide useful insight into how the various multinary compounds form. Several thiophosphate groups such as $[PS_4]^{3-}$,[5] $[P_2S_6]^{4-}$,[6] $[P_2S_6]^{2-}$,[6b] and $[P_2S_7]^{2-}$,[7] have been isolated and structurally characterized as their alkali metal or alkaline earth salts. Surprisingly, the corresponding selenophosphate anions are much less studied, and only $[P_2Se_9]^{4-}$ [3b] has been recently structurally characterized. In this context, we report herein on the flux synthesis, structure, and properties of the $[P_8Se_{18}]^{6-}$ anion. Its structure and composition are surprising in that it is a mixed-valent species with P^{4+} and P^{3+} centers. The latter were thought to be unstable in polyselenophosphate fluxes.

Experimental Section

Reagents. The reagents mentioned in this study were used as obtained unless noted otherwise: red phosphorus powder, Morton Thiokol, Inc., −100 mesh, Danvers, MA; potassium metal, analytical reagent, Johnson Matthey/AESAR Group, Seabrook, NH; selenium powder, 99.5+% purity, −100 mesh, Aldrich Chemical Co., Inc., Milwaukee, WI.

Syntheses. K_2Se was prepared by reacting stoichiometric amounts of the elements in liquid ammonia as described elsewhere.[3a]

Single crystals of $K_6P_8Se_{18}$ were first obtained from a mixture of TiO_2 (0.30 mmol), P_2Se_5 (0.60 mmol), and K_2Se (0.60 mmol) which was heated in an evacuated Pyrex tube to 510 °C for 3 days, followed by cooling to 50 °C at 4 °C h^{-1}. The excess $K_xP_ySe_z$ flux was removed with DMF. Further washing with anhydrous ether revealed an intimate mixture of orange rod-like crystals of $K_6P_8Se_{18}$ (∼40%) and black rod-like crystals of $KTiPSe_5$ (∼60). This serendipitous synthesis allowed the single-crystal structure to be determined, which in turn allowed a rational synthesis as follows: A mixture of K_2Se (0.45 mmol), P (1.20 mmol), and Se (2.25 mmol) was heated in an evacuated Pyrex tube to 510 °C for 2 days, followed by cooling to 50 °C at 10 °C h^{-1}. The product was washed with DMF and anhydrous ether, to give pure orange microcrystals of $K_6P_8Se_{18}$ (∼87% yield based on P). The crystals are air- and water-sensitive. Semiquantitative microprobe analysis gave a composition of $K_{5.7}P_{7.6}Se_{18.4}$.

Physical Measurements. *Powder X-ray diffraction* analyses were performed using a calibrated Rigaku-Denki/RW400F2 (Rotaflex) rotating anode powder diffractometer controlled by an IBM computer, operating at 45 kV/100 mA and with a 1 deg/min scan rate, employing Ni-filtered Cu radiation. *Infrared spectra*, in the far-IR region (600−50 cm^{-1}), were recorded on a computer-controlled Nicolet 750 Magna-IR Series II spectrophotometer equipped with a TGS/PE detector and silicon beam splitter in 4 cm^{-1} resolution. *Optical diffuse reflectance* measurements were performed as described elsewere.[2,3] *Differential thermal analysis* experiments were performed on a computer-controlled Shimadzu DTA-50 thermal analyzer. To evaluate congruent melting we compared the X-ray powder diffraction patterns before and after the DTA experiments. The stability and reproducibility of the samples were monitored by running multiple heating/cooling cycles. *Semiquantitative microprobe analyses* were performed using a JEOL JSM-6400V scanning electron microscope (SEM) equipped with a TN 5500 EDS detector.

X-ray Structure Determination. A Rigaku AFC6S diffractometer equipped with a graphite crystal monochromator and Mo Kα (λ = 0.710 69 Å) radiation was used to collect data from a crystal of 0.39 × 0.08 × 0.05 mm dimensions in an $\omega - 2\theta$ scan mode. The structure was solved with SHELXS-86[8a] and refined by full-matrix least-squares techniques of the TEXSAN[8b] package of crystallographic programs. Crystal data at 23 °C: $a = 9.746(2)$ Å, $b = 8.332(1)$ Å, $c = 23.054(4)$ Å, $\beta = 90.54(1)^\circ$, $V = 1872.1(5)$ Å^3, $Z = 2$, $D_c = 3.377$ g cm^{-3}, space group $P2_1/n$ (No. 14), μ(Mo Kα) = 185.47 cm^{-1}, $2\theta_{max} = 45.0^\circ$, octants collected $0 < h < 12$, $0 < k < 10$, $-27 < l < 27$; number of total data collected, 2828; unique data, 2647 ($R_{int} = 0.072$); data with $F_o^2 > 3\sigma(F_o^2)$, 1056. Number of variables: 146. An empirical absorption correction based on ψ scans and a decay correction (−9.8%) were applied to the data; ratio of absorption coefficients (min/max): 0.543. All atoms were refined anisotropically. Final $R/R_w = 0.037/0.040$.

Results and Discussion

$K_6P_8Se_{18}$ contains the new discrete $[P_8Se_{18}]^{6-}$ anion. Each anion can be viewed as the result of the fusion of three $[P_2Se_6]$ and two $[PSe_3]$ fragments, linked in an alternating fashion; see Figure 1. In this respect the molecule is an oligomeric unit, which consists of four $[P_yQ_z]^{n-}$ subunits. The most intriguing feature of the molecule is the presence of the $[PSe_3]$ pyramidal fragments. These units are observed for the first time and are

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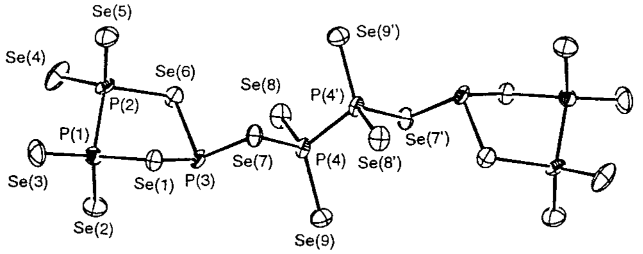

Figure 1. ORTEP representation and labeling of a single $[P_8Se_{18}]^{6-}$ anion 60% ellipsoids). Selected distances (Å) are as follows: P(1)−Se(1) 2.271(7), P(1)−Se(2) 2.142(7), P(1)−Se(3) 2.129(7), P(2)−Se(4) 2.123(7), P(2)−Se(5) 2.136(7), P(2)−Se(6) 2.300(6), P(3)−Se(1) 2.281(7), P(3)−Se(6) 2.321(7), P(3)−Se(7) 2.275(7), P(4)−Se(7) 2.297(7), P(4)−Se(8) 2.135(6), P(4)−Se(8) 2.149(7), P(1)−P(2) 2.253(9), P(4)−P(4′) 2.25(1). Selected angles (deg) are as follows: Se(1)−P(1)−Se(2) 110.4(3), Se(1)−P(1)−Se(3) 108.6(3), Se(1)−P(1)−P(2) 97.7(3), Se(4)−P(2)−Se(5) 115.8(3), Se(4)−P(2)−Se(6) 111.5(3), Se(4)−P(2)−P(1) 106.8(3), Se(1)−P(3)−Se(6) 103.6(2), Se(1)−P(3)−Se(7) 88.5(2), Se(6)−P(3)−Se(7) 107.7(3), Se(7)−P(4)−Se(8) 109.9(3), Se(7)−P(4)−Se(9) 112.4(3), Se(7)−P(4)−P(4′) 93.9(4), P(1)−Se(1)−P(3) 91.3(2), P(2)−Se(6)−P(3) 101.6(2), P(3)−Se(7)−P(4) 90.1(2).

composed of phosphorus in a trigonal pyramidal coordination with three selenium atoms. The formal charge of the phosphorus atoms in these units is 3+ with the apex of the pyramid occupied by the lone pair. The sulfur analogue $[PS_3]^{3-}$ unit has been observed bound to a transition metal in $P_{0.2}VS_2$,[9] which is structurally characterized only with X-ray and neutron powder diffraction data. The infinite (1/00) $[P_3Se_4^{-}]$ also features a pyramidal P^{3+} atom coordinated to a Ru^{2+} center via its lone pair,[3e] whereas the organic compound $P(SeC_6H_5)_3$ contains a PSe_3 unit bonded to three phenyl rings via the selenium atoms.[10]

In addition to the PSe_3 moieties, the $[P_8Se_{18}]^{6-}$ anion also contains one bridging and two terminal $[P_2Se_6]$ fragments, Figure 1. These fragments have tetrahedral P^{4+} atoms, and they possess the familiar ethane-like conformation which is observed for the $[P_2Se_6]^{4-}$ ligand.[2a−d,3a,c,f,g,4a] Each terminal unit [i.e., P(1)−P(2)] employs two Se atoms to share with the pyramidal P^{3+} atoms [i.e., P(3)] in a chelating fashion. This results in a skew five-membered ring [Se(1)−P(1)−P(2)−Se(6)−P(3)]. The Se(1)−P(1)−P(2)−Se(6) torsion angle of 55.3(3)° is significantly smaller than the Se(7)−P(4)−P(4′)−Se(9′) of 63.9(4)°. The bridging $[P_2Se_6]$ unit [i.e., P(4)−P(4′)] links the two pyramidal phosphorus atoms by sharing one Se atom with each one. The arrangement of the molecule is such that the two $[PSe_3]$ pyramids face at opposite directions. There is a center of symmetry situated in the middle of the P−P bond of the central $[P_2Se_6]$ unit, Figure 1.

Interestingly, some intra- and intermolecular Se−Se interactions are observed between the different $[P_8Se_{18}]^{6-}$ molecules in the cell. The most significant intermolecular interaction is between Se(1) and Se(5) at 3.300(4) Å (van der Waals radii sum is 3.8 Å).[11] This interaction affects the packing of the molecules to a great extent, forcing them into a "step-like" pseudolamellar packing, Figure 2A. In the absence of an electronic structure calculation, it is not possible to assess whether this close Se−Se contact has a bonding character. Within the corrugated layer each molecule interacts with four neighboring ones to form a perforated net with rings occupied by the K^+ cations, Figure 2B. Furthermore, Se(1) also engages in an intramolecular interaction with Se(7) at 3.180(3) Å [Se(6)−Se(7), 3.712(3) Å]. There are three different environments for the K atoms; K(1) is five-coordinate [range of K−Se distances, 3.539(7)−3.655(7) Å; average 3.592 Å], K(2) is six-coordinate [range of K−Se distances, 3.206(7) −3.697(7) Å; average 3.485 Å] and has a close K(2)−P(3) contact at 3.280(9) Å, and K(3) is nine-coordinate [range of K−Se distances, 3.510(7)−3.734(6) Å; average 3.585 Å]. Other selected distances and angles are given in the Figure 1 caption.

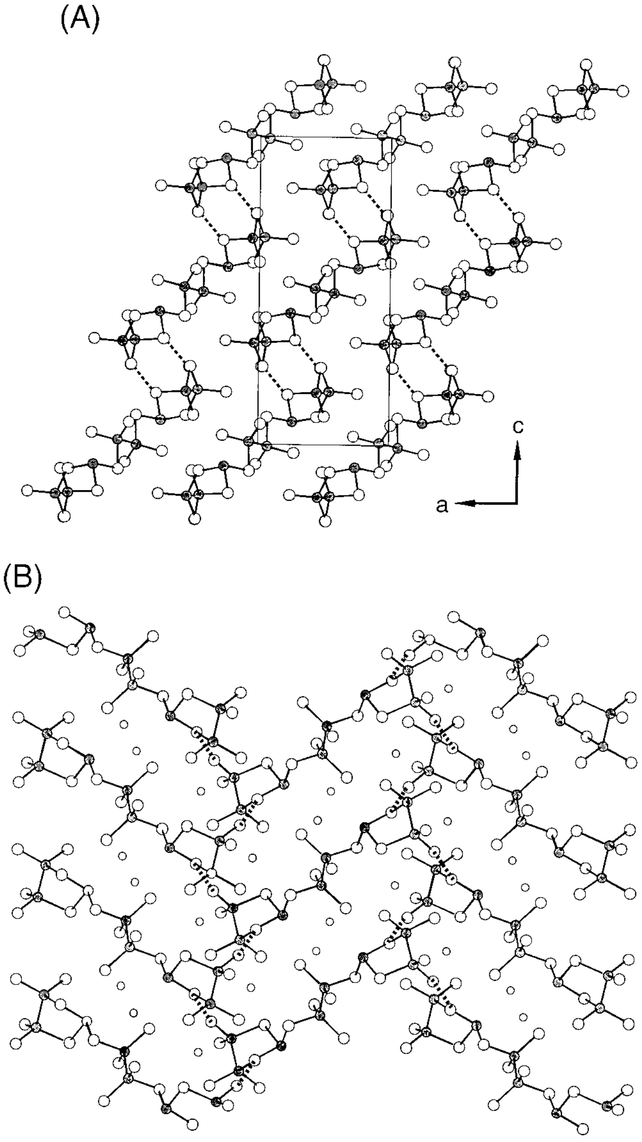

Figure 2. (A) The unit cell of $K_6P_8Se_{18}$ viewed down the *b*-axis. Potassium cations were omitted for clarity. Dashed lines indicate Se(1)−Se(5) interactions at 3.300(4) Å. (B) Stick model of the pseudolayer as viewed along the [6 0 $\bar{1}$] direction. Dashed lines indicate Se(1)−Se(5) interactions.

$K_6P_8Se_{18}$ is insoluble in methanol, acetonitrile, and DMF, but slowly soluble in a solution of crown ether, 18-crown-6, in DMF. The solution is yellowish, and its UV/vis spectrum features a shoulder at ~390 nm (3.18 eV). Single-crystal optical transmission spectroscopy performed on $K_6P_8Se_{18}$ shows a sharp optical gap, E_g, of 2.33 eV. The infrared spectrum displays absorptions at ca. 517 (m), 507 (s), 489 (s), 430 (m), 413 (m), 403 (m), 369 (m), 352 (s), 332 (s), 289 (s), and 276 (w) cm^{-1} that should be characteristic in distinguishing the $[P_8Se_{18}]^{6-}$ from other $[P_yQ_z]^{n-}$ units. The vibrations at ca. 507, 489, 430, 403,

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and 369 cm^{-1} are very close to values observed for PSe_3 stretching modes of the $[P_2Se_6]^{4-}$ ligand.[3a,c,f,4a] Differential thermal analysis (DTA) shows that $K_6P_8Se_{18}$ melts congruently at ca. 421 °C.

A new and unusual flux constituent $[P_yQ_z]^{n-}$ anion with an unexpected molecular structure has been synthesized. The molecule features $[PSe_3]$ pyramidal fragments observed for the first time. The novel packing of the molecules is predominated by Se−Se interactions which result in the formation of pseudolayers. The isolation and identification of the $[P_8Se_{18}]^{6-}$ anion enriches our understanding and insight about the kinds of species present inside the molten selenophosphate fluxes and suggests that, beyond the ordinary $[PSe_4]^{3-}$ and $[P_2Se_6]^{4-}$, oligomeric $[P_yQ_z]^{n-}$ species can also be stabilized. Given that $K_6P_8Se_{18}$ melts congruently, it would be interesting to investigate if it can be useful as a starting material (or as a flux) for the formation of quaternary $A_nM_xP_yQ_z$ compounds (A = alkali metal, M = metal).[12]

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Supporting Information Available: Table of crystallographic details, fractional atomic coordinates of all atoms, anisotropic and isotropic thermal parameters of all atoms, interatomic distances and angles, and calculated and observed X-ray powder pattern (19 pages). Ordering information is given on any current masthead page.

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