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# $\alpha$-$Na_6Pb_3(PS_4)_4$, a Noncentrosymmetric Thiophosphate with the Novel, Saucer-Shaped $[Pb_3(PS_4)_4]^{6-}$ Cluster, and Its Metastable, 3-Dimensionally Polymerized Allotrope $\beta$-$Na_6Pb_3(PS_4)_4$

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Polychalcophosphate fluxes are now a well-established tool for preparing new ternary and quaternary thio- and selenophosphate compounds.[1−4] In these fluxes well-defined, discrete $[P_yQ_z]^{n-}$ fragments are stabilized and act as ligands to metal cations forming solids with structures of every dimensionality. After our success in synthesizing new quaternary compounds in the $M/A_2Se/P_2Se_5/Se$ (M = Pb, Eu and A = K, Rb, Cs) systems,[5] we decided to explore the Li and Na congeners. In general it is more challenging to obtain compounds containing Li and Na because, as the size of the alkali metal decreases, the basicity of the flux decreases along with the probability that they will be incorporated into the product.[6] Yet, this proved successful for $LiEuPSe_4$[5b] and $Na_{1.5}Pb_{0.75}PSe_4$.[7] Because the corresponding sulfur systems generally behave differently (primarily due to the dissimilar redox behavior of the $P^{5+}/P^{4+}$ couple in a sulfur environment), we investigated the Na/Pb/P/S system. Here we report on $\alpha$-$Na_6Pb_3(PS_4)_4$ a noncentrosymmetric thiophosphate featuring the novel, saucer-shaped $[Pb_3(PS_4)_4]^{6-}$ cluster with an unusual $\mu_4$-sulfide anion in a *flattened umbrella-like* geometry. Also, we report on its metastable allotrope $\beta$-$Na_6Pb_3(PS_4)_4$. The $\beta$-phase adopts the structure of $Na_{1.5}Pb_{0.75}PSe_4$[7] and has an astonishing structural relationship to the $\alpha$-phase.

$\alpha$-$Na_6Pb_3(PS_4)_4$ can be obtained as yellow needles from a sodium thiophosphate flux as well as a microcrystalline powder from a stoichiometric reaction of the starting materials.[8a] $\beta$-$Na_6Pb_3(PS_4)_4$ can be prepared as a powder by the stoichiometric reaction of the starting materials followed by rapid quenching.[8b] The $\beta$-phase is metastable and converts to the $\alpha$-phase upon heating.[9] The hint to us that a structural relationship existed between these two phases was in the X-ray powder diffraction patterns. The pattern of the $\beta$-phase overlaps almost perfectly with that of the $\alpha$-phase except for the fact that a number of Bragg peaks are missing (due to the higher symmetry of the $\beta$-phase).

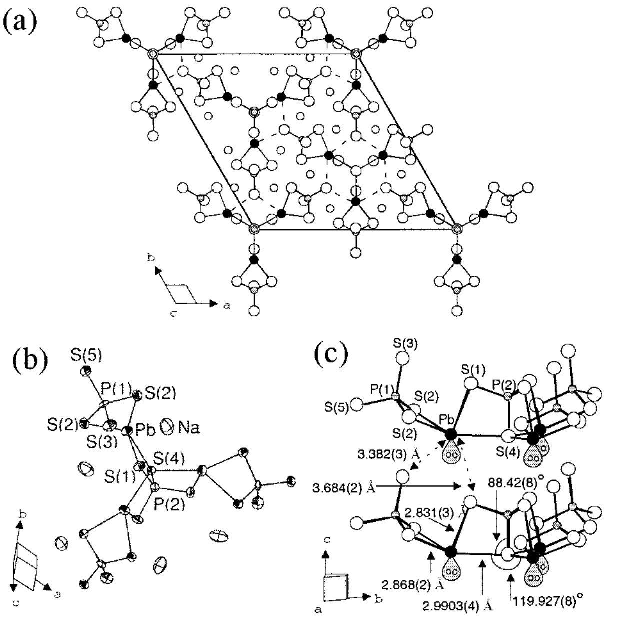

**Figure 1.** (a) The structure of $\alpha$-$Na_6Pb_3(PS_4)_4$ looking down the *c*-axis. The closest intercluster approach is 3.223(1) Å, shown by dashed lines. Na atoms are small, open circles; Pb atoms are black; P atoms are gray circles; and S atoms are large, open circles. (b) ORTEP representation of the $[Pb_3(PS_4)_4]^{6-}$ molecule found in $\alpha$-$Na_6Pb_3(PS_4)_4$ surrounded by $Na^+$ cations, shown with thermal vibrational (90%) ellipsoids. (c) A view of two adjacent $[Pb_3(PS_4)_4]^{6-}$ molecules down the *a*-axis.

$\alpha$-$Na_6Pb_3(PS_4)_4$[10] consists of discrete trigonally packed $[Pb_3(PS_4)_4]^{6-}$ cluster molecules surrounded by $Na^+$ counterions, see Figure 1a. Each molecule is situated on a *3mm* symmetry site and is composed of 4 $PS_4$ tetrahedra and 3 $PbS_4$ polyhedra, see Figure 1b. The coordination environment of the Pb atoms can be best described as a trigonal bipyramid with one axial ligand removed. The central $P(2)S_4$ tetrahedron edge shares with three $PbS_4$ polyhedra. Each $Pb^{2+}$ ion is chelated by two $[PS_4]^{3-}$ ligands.

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(8) (a) $\alpha$-$Na_6Pb_3(PS_4)_4$ was obtained from the reaction of $Pb/P_2S_5/Na_2S/S$ (1:2:3:8) that was sealed under vacuum ($\sim 2 \times 10^{-4}$ mbar) in a Pyrex tube and heated to 500 °C for 4 days followed by cooling to 250 °C at 2 °C $h^{-1}$. The excess $Na_xP_yS_z$ flux was removed with DMF to reveal yellow needles that decompose slowly in air and $H_2O$. The compound was also prepared as a crystalline powder (with <5% PbS contamination) from a stoichiometric mixture of $Pb/P_2S_5/Na_2S/S$ (3:2:2:3) that was sealed under vacuum and heated to 680 °C for 12 h followed by cooling to 250 °C at 10 °C $h^{-1}$. (b) $\beta$-$Na_6Pb_3(PS_4)_4$ was prepared as a yellow crystalline powder (with <5% PbS contamination) by rapid quenching of a stoichiometric mixture of $Pb/P_2S_5/Na_2S/S$. A few small, single crystals, which decomposed slowly in air and $H_2O$, were found.

(9) Differential thermal analysis (DTA) of $\beta$-$Na_6Pb_3(PS_4)_4$ (10 °C/min heating/cooling rate, atmosphere = vacuum) and the X-ray diffraction pattern of the product obtained after DTA show that $\beta$-$Na_6Pb_3(PS_4)_4$ melts at ~580 °C and on cooling transforms to $\alpha$-$Na_6Pb_3(PS_4)_4$ along with some PbS. X-ray diffraction of the product after DTA of the $\alpha$-phase shows the $\alpha$-phase and precipitated PbS. Annealing of the $\beta$-phase at 375 °C for 2 days also converts it to the $\alpha$-phase.

(10) (a) Crystal data at −100 °C: Bruker SMART diffractometer, Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å), $R3m$, $a = 19.4527(2)$ Å, $c = 6.1720(1)$ Å, $V = 2022.63(4)$ Å$^3$, $Z = 3$, $D_c = 3.439$ g cm$^{-3}$, yellow needle, $0.52 \times 0.06 \times 0.05$ mm, $\mu = 20.253$ mm$^{-1}$, $2\theta_{max} = 54°$, 4975 total reflections, 1065 unique reflections with $R(\text{int}) = 0.042$, refinement on $F^2$, GOF = 1.175, 55 parameters, R1 = 1.96% and wR2 = 4.96% for $I > 2\sigma(I)$. An empirical absorption correction was done using SADABS,[10b] and all atoms were refined anisotropically. (b) Bruker Analytical X-ray Instruments Inc., Madison, WI.

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The structure is polar because the saucer-shaped molecules stack along the *c*-axis pointing in the same direction, see Figure 1c. The lone pair of electrons from the Pb atoms are, presumably, stereochemically expressed on the convex side of the saucer and point toward the concave side of the neighboring molecule along the *c*-axis. The closest intercluster approach is through two long Pb−S distances of 3.223(1) Å, see Figure 1a. It is possible that these long interactions are significant in the stabilization of this phase.

One rather unique feature of the structure is the highly unusual bonding environment of S(4), which is bonded to three Pb atoms and one P atom to make a flattened umbrella-like geometry, see Figure 1c. The S(4) atom is located only 0.08 Å below the plane of the three Pb atoms. This geometry is most probably a consequence of the $Pb^{2+}$ coordination sphere and the stereochemical expression of its lone pair. The bonding environment of S(4) can be compared with those of the mineral sulvanite, $Cu_3VS_4$[11] and $Na_6Cd_7S_{10}$[12] which have a normal umbrella-like geometry. In these cases the S atoms lie above the plane of the three metal atoms, ∼0.6 Å.

We were surprised to find that quenching a melt of the $Na_6Pb_3(PS_4)_4$ stoichiometry resulted in a metastable compound[13] with the same stoichiometry but a 3-dimensionally connected framework found earlier in $Na_{1.5}Pb_{0.75}PSe_4$. A comparison of both phases (down the *c*-axis of the α-phase and the body diagonal of the *β*-phase) shows that the two structures are in fact related, see Figure 2a,b. It is apparent that the $[PS_4]^{3-}$ tetrahedra are similarly arranged in both structures; however, they differ in relative orientation through slight rotations or even flips. These movements of the tetrahedra are accompanied by segregation of the Na and Pb cations. The cubic *β*-phase displays Na/Pb disorder in some sites whereas the rhombohedral α-phase is well-ordered. The higher symmetry and presence of disorder in the *β*-phase are consistent with the fact that it is metastable and of higher entropy.

An important difference between *β*- and α-$Na_6Pb_3(PS_4)_4$ is the coordination environment of Pb. In the *β*-phase the Pb atoms are still 4-coordinate;[14] however, they are now chelated by four $[PS_4]^{3-}$, instead of only two, which makes the structure 3-dimensional, see Figure 2c,d. S(1) in the *β*-phase has a coordination sphere similar to that of S(4) in the α-phase. However, since S(1) is located 0.45 Å below the plane of the three Pb/Na atoms, its environment is closer to an *inverted umbrella* or a distorted tetrahedron.

Overall, we can view *β*-$Na_6Pb_3(PS_4)_4$ as a metastable structure in which the saucer-shaped clusters are linked (i.e., polymerized) by intercluster Pb···S interactions that result in a different coordination for Pb. This process contracts the unit cell volume by 4%, yielding the denser *β*-phase. In this context the latter can be regarded as a "high-pressure" form. Figure 2d shows what used to be the saucer-shaped molecules. The central $[PS_4]^{3-}$ units in these stacked molecules have been flipped below the plane of the three Pb/Na atoms so that they now serve to link the clusters along the columnar stack.

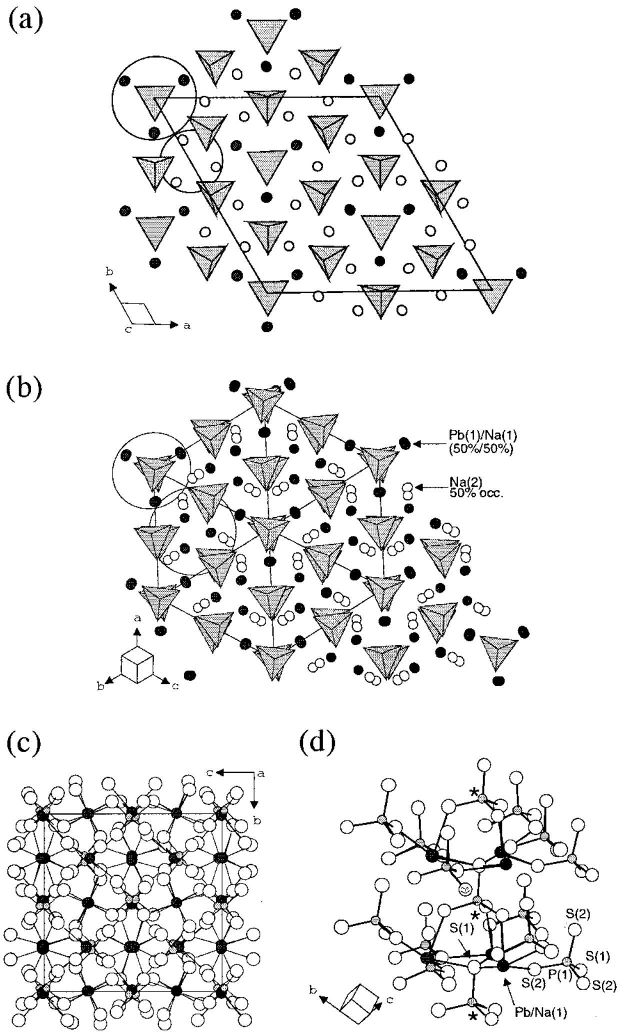

**Figure 2.** A comparison of (a) α-$Na_6Pb_3(PS)_4$ viewed down the *c*-axis and (b) *β*-$Na_6Pb_3(PS_4)_4$ viewed down the body diagonal. Pb−S bonds have been omitted for clarity. In both structures two groups of cations have been circled so that one can see the correspondence from one structure to the other. (Na(2) in the *β*-phase cannot be more than 50% occupied since a symmetry equivalent atom is generated 0.82(1) Å away.) (c) The *β*-phase with Pb−S bonds drawn. Na(2) has been omitted for clarity. (d) A fragment of the *β*-phase that can be compared to that in Figure 1c. The asterisk (*) indicates the tetrahedra that have flipped.

α- and *β*-$Na_6Pb_3(PS_4)_4$ exhibit sharp optical absorptions at ∼2.7 and 2.57 eV, respectively. This is consistent with the fact that generally molecular structures have greater energy gaps than their polymeric allotropes (i.e., red and black Se). The small energy difference for these two phases may indicate that the observed excitations are in fact local in nature involving S→P charge-transfer transitions.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) (a) Crystal data at −100 °C:_ Bruker SMART diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å), $I\bar{4}3d$, $a = 13.730(2)$ Å, $V = 2588.1(7)$ Å$^3$, $Z = 16$, $D_c = 3.584$ g cm$^{-3}$, yellow plate, $0.20 \times 0.10 \times 0.02$ mm, $\mu = 21.104$ mm$^{-1}$, $2\theta_{max} = 54°$, 9019 total reflections, 483 unique reflections with $R(\text{int}) = 0.079$, refinement on $F^2$, GOF = 1.162, 24 parameters, R1 = 3.02% and wR2 = 6.81% for $I > 2\sigma(I)$. The structure was solved and refined in the same manner as those in ref 7.

(14) The coordination environment of the Pb can be described as a distorted *seesaw* (octahedral with two axial ligands removed). However, when this site is occupied by Na, which is half of the time, the coordination number is 8.