

Coordination Chemistry of $[P_2Se_6]^{4-}$ in Molten Fluxes. Isolation of the Structurally Complex KMP_2Se_6 ($M = Sb, Bi$)

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The layered compounds, KMP_2Se_6 ($M = Sb, Bi$), have been prepared by the reaction of Bi(Sb) with a molten alkali-metal polyselenophosphate flux.

Recently, we reported the synthesis of new quaternary metal thiophosphate compounds ($ABiP_2S_7$; $A = K, Rb$) using molten alkali polythiophosphate fluxes at intermediate temperatures.¹ We have extended this methodology to new quaternary metal selenophosphates, because the chemistry of selenophosphate ligands is not well developed. The rare $[PSe_4]^{3-}$ ligand is found in solid-state compounds such as Cu_3PSe_4 ² and Tl_3PSe_4 ,³ and in the unusual tungsten complex, $[WSe(PSe_2)(PSe_4)]^{2-}$, which also contains the unprecedented heteroallylic $[PSe_2]^-$ unit.⁴ Most of the known solid-state selenophosphates contain the ethane-like $[P_2Se_6]^{4-}$ ligand, as for example in the important $M_2P_2Q_6$ ($Q = S, Se$) family of compounds.^{5,6} Thus far, transition metals have received the most attention in this system although a few examples with main group elements such as Sn,⁷ Pb,⁷ and In⁸ are known. Recently, several mixed-metal selenophosphates of the $M_2P_2Q_6$ family have been prepared.⁹ It is noteworthy that $In_{1.33}P_2Se_6$ may be suitable for photovoltaic devices.¹⁰ These compounds are typically synthesized by direct combination of the elements at 500–800 °C. Studies have shown that the $M_2P_2Q_6$ structural type is very thermodynamically stable. In order to explore new metal-selenophosphates at lower temperatures and to obtain new structure types we adopted the flux technique using the polyselenophosphate $A_x[P_ySe_z]$ fluxes at <600 °C. A key feature of these melts is that they are Se-rich. The $A_x[P_ySe_z]$ fluxes provide excess $[P_ySe_z]^{n-}$ anions which bind to metal ions and act as mineralizers. They also provide a strong basic medium which discourages the formation of $M_2P_2Se_6$. We highlight that $A_x[P_ySe_z]$ fluxes behave significantly differently than their sulfur analogues and stabilize readily $[P_2Se_6]^{4-}$ units. This results in solid-state compounds with no sulfur analogues. The synthesis,[†] structural characterization, optical and thermal properties of two new isostructural quaternary compounds, KMP_2Se_6 ($M = Bi, Sb$), are reported. They feature a novel layered structure containing the $[P_2Se_6]^{4-}$ building block in a complex bonding mode.

KMP_2Se_6 has the complicated layered structure shown in Fig. 1.‡ The layers are separated by seven-coordinate K^+ ions [$K-Se$ mean 3.36(2) Å]. The $[MP_2Se_6]^-$ slabs are assembled from chains of distorted corner-sharing $BiSe_6$ octahedra along the b -axis [Fig. 2(a)]. The $[P_2Se_6]^{4-}$ ligand trichelates to one Bi while a fourth Se atom acts as a bridge between two other Bi atoms in the chain. The fifth Se is non bonding while the sixth Se connects to a Bi on the neighbouring chain to form a

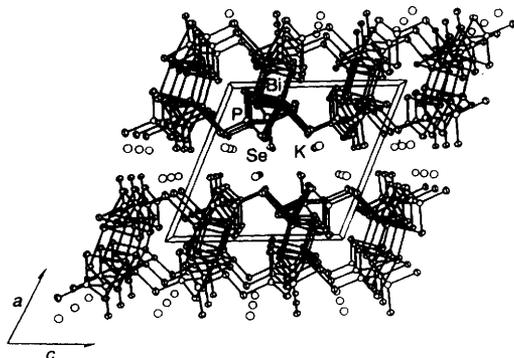


Fig. 1 The extended structure of $KBiP_2Se_6$, looking down the b -axis

layer in the bc -plane (Fig. 1). For clarity, the unique connectivity of $[P_2Se_6]^{4-}$ is illustrated separately in Fig. 3.

Bismuth is coordinated by six Se atoms to form a distorted octahedron. The Bi-Se distances range from 2.821(2) to 3.194(3) Å. The distortion of the octahedron can partly be explained by the stereochemically active $6s^2$ lone pair of Bi^{3+} . The Bi-Se coordination sphere is shown in Fig. 2(b). In accordance with the VSEPR model,¹¹ lone pair-bond pair repulsions in the bismuth coordination sphere result in longer bond lengths for those bonds adjacent to the lone pair [Bi-

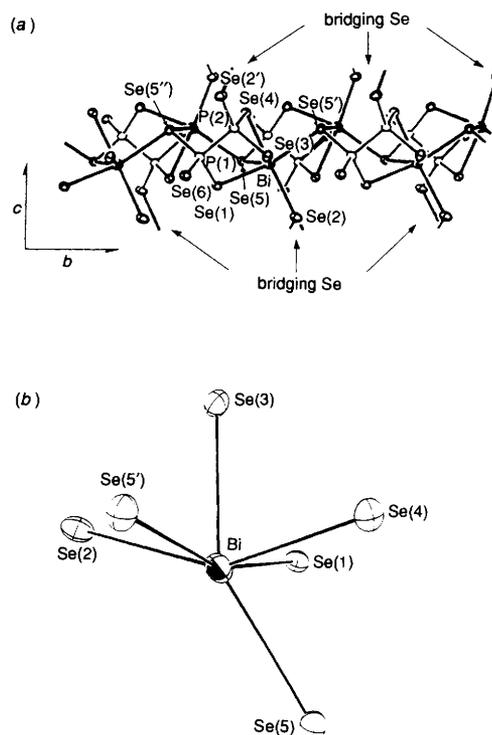


Fig. 2 (a) Structure and labelling of a $[BiP_2Se_6]^-$ chain. The bridging Se atoms connecting the chains into layers are highlighted. Selected distances (Å) are as follows: Bi-Se(1) 2.878(2), Bi-Se(2) 3.194(3), Bi-Se(3) 2.873(2), Bi-Se(4) 2.821(2), Bi-Se(5) 3.131(2), Bi-Se(5') 3.079(2), P(1)-P(2) 2.238(7), P(1)-Se(1) 2.223(5), P(1)-Se(5') 2.198(6), P(1)-Se(6) 2.145(5), P(2)-Se(2') 2.146(5), P(2)-Se(3) 2.197(6), P(2)-Se(4) 2.221(6). Selected angles (°) are as follows: Se(1)-Bi-Se(3) 83.17(6), Se(3)-Bi-Se(4) 76.37(6), Se(2)-Bi-Se(5) 126.07(6), Se(3)-Bi-Se(5) 147.91(7), Se(4)-Bi-Se(5) 81.39(6), Se(5)-Bi-Se(5') 118.32(5), Bi-Se(1)-P(1) 100.6(2), Se(5')-P(1)-Se(6) 113.0(3), Se(6)-P(1)-Se(1) 115.5(2), Se(1)-P(1)-P(2) 104.0(3), Se(3)-P(2)-Se(4) 105.7(2), Se(2')-P(2)-Se(4) 115.9(2). (b) The Bi-Se coordination site with labelling.

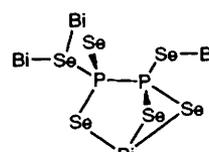


Fig. 3

Se(2,5,5') 3.079(2)–3.194(3) Å and shorter lengths for those more remote [Bi–Se(1,3,4) 2.821(2)–2.878(2) Å]. In addition, these repulsions give rise to an opening of the bond angles straddling the lone pair [Se(5)–Bi–Se(5') 118.32(5)°, Se(2)–Bi–Se(5) 126.07(6)°].

The P(1)–P(2) bond in $[P_2Se_6]^{4-}$ is 2.238(7) Å.

The optical properties of $KBiP_2Se_6$ and $KSbP_2Se_6$ suggest that they are wide band-gap semiconductors. The optical absorption spectrum shown in Fig. 4(a) indicates that $KBiP_2Se_6$ is optically transparent below the band gap E_g of 1.61 eV. The E_g of $KSbP_2Se_6$ is found to be 2.00 eV, Fig. 4(b).

Differential thermal analysis (DTA) shows that $KBiP_2Se_6$ and $KSbP_2Se_6$ melt congruently at 554 and 479 °C respectively.

The difference between the sulfur and selenium chemistry in these quaternary systems is partly due to the difference in oxidizing ability of the excess polychalcogenide ligands in these fluxes. In this temperature range polythiophosphate fluxes yield $[P_2S_7]^{4-}$ and $[PS_4]^{3-}$ ligands with P in the 5+ oxidation state whereas the polyselenophosphate fluxes stabilize the $[P_2Se_6]^{4-}$ unit with P in the 4+ oxidation state. This leads to entirely different structural chemistry.

In conclusion, the synthesis of new quaternary selenophosphates with A/P/Se molten salts will be a productive synthetic approach with broad scope. For example, a number of other new A/M/P₂Se₆ (A = K, Rb, Cs; M = Sb, Bi, Mn, Fe) compounds have been synthesized with this method and structurally characterized.¹³ The $A_x[P_ySe_z]$ fluxes provide reliably $[P_2Se_6]^{4-}$ units for coordination to metal ions. The

high negative charge of these units makes them hard to stabilize in conventional aqueous or organic solvents.

Financial support from the National Science Foundation DMR-9202428, is gratefully acknowledged.

Received, 22nd October 1993; Com. 3/06329A

Footnotes

† $KBiP_2Se_6$ was synthesized from a mixture of Bi (0.15 mmol), P_4Se_{10} (0.225 mmol), K_2Se (0.3 mmol), and Se (1.2 mmol) that was sealed under vacuum in a Pyrex tube and heated to 410 °C for 4 d followed by cooling to 110 °C at 4 °C h⁻¹. The excess deep red $K_xP_ySe_z$ matrix was removed with DMF to reveal analytically pure dark red plate-like crystallites of $KBiP_2Se_6$ (69% yield). The crystals are air- and water-stable. Single crystals of the Sb analogue were synthesized as above, except at 450 °C for 6 d (75% yield). The compound is X-ray isomorphous to $KBiP_2Se_6$.

‡ Crystal data for $KBiP_2Se_6$ at 23 °C: $a = 12.403(5)$, $b = 7.595(2)$, $c = 12.412(3)$ Å, $\beta = 111.58(3)^\circ$, $V = 1087(1)$ Å³, $Z = 4$, $D_c = 4.788$ g cm⁻³, space group $P2_1/c$ (no. 14), $\mu(Mo-K\alpha) = 366.75$ cm⁻¹, $2\theta_{max} = 50^\circ$, total data collected, 2170; unique data, 2070; data with $F_o^2 > 3\sigma(F_o^2)$, 1228. An empirical absorption correction based on ψ scans was applied to the data, followed by a (DIFABS)¹⁴ correction to the isotropically refined data. Complete anisotropic refinement (92 variables) resulted in a final $R/R_w = 0.039/0.045$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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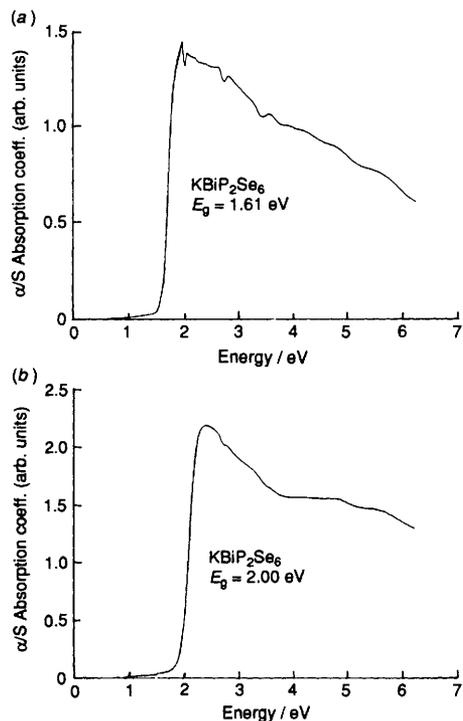


Fig. 4 Solid-state optical absorption spectra of (a) $KBiP_2Se_6$ and (b) $KSbP_2Se_6$