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$A_2AuP_2Se_6$ (A = K, Rb): Mixed-Valent Compounds with All Possible Coordination Geometries for Gold

Konstantinos Chondroudis, Timothy J. McCarthy, and Mercouri G. Kanatzidis*

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

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Recently, we showed that the polychalcophosphate fluxes are eminently useful for the synthesis of new ternary and quaternary thiophosphate and selenophosphate complexes.[1] These fluxes are formed by *in situ* fusion of $A_2Q/P_2Q_5/Q$ and contain $[P_yQ_z]^{n-}$ ligands (Q = S, Se) which, in the presence of metal ions, coordinate to give interesting new materials. We have demonstrated that novel solid state structures can be constructed from $[P_2Q_7]^{4-}$, $[PQ_4]^{3-}$, $[P_2Se_6]^{4-}$, $[P_2Se_9]^{4-}$, etc.[2−5] These include $ABiP_2S_7$ (A = K,Rb),[2a] KMP_2Se_6 (M = Sb,Bi),[2b] $Cs_8M_4(P_2Se_6)_5$ (M = Sb,Bi),[3a] $A_2MP_2Se_6$,[3b] $APbPSe_4$,[4a] $A_4Pb(PSe_4)_2$ (A = Rb,Cs),[4a] $K_4Eu(PSe_4)_2$,[4a] $A_4Ti_2(P_2Se_9)_2(P_2Se_7)$,[4b] $ATiPSe_5$,[4b] and $K_2UP_3Se_9$.[4c] In this context, the recently reported $KLaP_2Se_6$ is also noteworthy.[5] In this family of compounds, gold is exceptional in that, to date, no structurally characterized compounds have been reported. Here we report the synthesis, structural characterization, and optical and thermal properties of the first selenophosphate quaternary gold compounds, $A_2AuP_2Se_6$ (A = K, Rb), which feature mixed valency, an unusual structure, and the presence of all possible coordination geometries for gold.

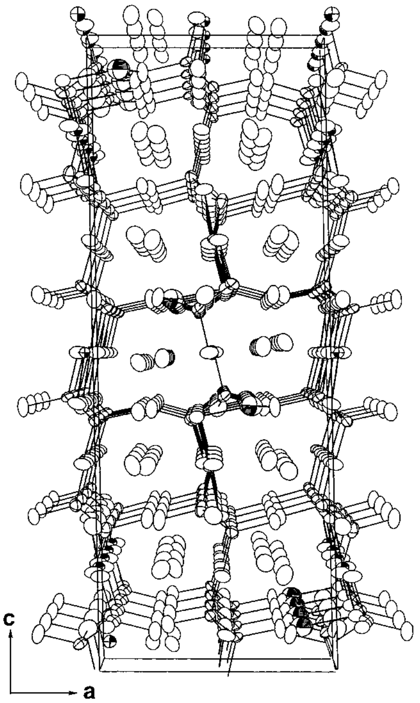

Figure 1. Unit cell of $A_2AuP_2Se_6$ viewed down the *b* axis. The packing of the chains in the unit cell forms channels where the A^+ cations are residing (open ellipses). In the infinite part of the structure, gold is shown as octant shaded ellipses, selenium as open ellipses, and phosphorus as crossed ellipses with no shading.

$A_2AuP_2Se_6$[6] is an unusual mixed-valent compound which, as it will become clear below, can be written as $A_6Au^{I}_{1.5}Au^{III}_{1.5}(P_2Se_6)_3$. Views of the structure along any axis give the impression of a three- or at least a two-dimensional material because of extensive overlap of the atoms (see Figure 1). The compound, in fact, possesses unique chains with a complicated one-dimensional sinusoidal structure. The chains feature the $[P_2Se_6]^{4-}$ group which acts as bridging multidentate ligand coordinating to four different gold atoms (see Figure 2). Each chain possesses two different crystallographic centers of symmetry residing in atoms Au(1) and Au(4). There are three types of $[P_2Se_6]^{4-}$ ligands in the structure. Each type coordinates to one, two, and three metal centers, respectively. The overall description of the one-dimensional structure can be characterized as a sinusoidal backbone with side groups attached to it, as illustrated in Figure 2. Atoms Au(1), Au(2), and Au(4) are part of the sinusoidal backbone, while atom Au(3) and its associated $[P_2Se_6]^{4-}$ group involving atoms P(3) and P(4) compose the side groups. Atoms Au(3) and Au(4) have square planar geometries and are assigned an oxidation state of +3. Atoms Au(1) and Au(2) are assigned an oxidation state of +1. The trigonal coordination for Au(2) is rare for this element. The largest angle is Se(2)−Au(2)−Se(13) at 137.16°, which is closer to the ideal 120° than to 180°, and supports the description of distorted trigonal planar geometry rather than a linear geometry with a 2+1 interaction. The only chalcogenide compound, that we are aware of, with an ideal trigonal coordination for gold is AAuTe(A = Na,K)[7] [Au−Te distance 2.682(1) Å].

The most unique feature of the structure is the presence of all the known coordination environments for Au.[8] The repeating unit, described above, gives rise to an infinite chain which propagates in a zigzag fashion along the [110] direction (Figure

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(6) (a) $A_2AuP_2Se_6$ (A = K,Rb) was synthesized from a mixture of Au (0.3 mmol), P_2Se_5(0.9 mmol), A_2Se (0.60 mmol), and Se (3 mmol) which was sealed under vacuum in a Pyrex tube and heated to 490 °C for 4 d, followed by cooling to 150 °C at 4 °C h^{-1}. The excess $A_xP_ySe_z$ flux was removed with DMF. The black, shiny, rodlike crystals are air- and water-stable (∼90% yield based on Au). Semiquantitative microprobe analysis on single crystals gave $K_{2.1}AuP_{1.8}Se_{5.9}$ and $Rb_2AuP_{1.7}Se_{6.2}$ (average on four data acquisitions). (b) The structure of the Rb salt was determined by X-ray single-crystal diffraction. The K salt diffracted well, but it did not yield suitable single crystals for a full crystallographic analysis. The powder pattern of the K salt indicated that it is isostructural with the Rb analog. The structure was solved with SHELXS-86[12a] and refined by full-matrix least-squares techniques of the TEXSAN[12b] package of crystallographic programs. 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 0.924 × 0.112 × 0.084 mm dimensions in an ω scan mode. Crystal data for $Rb_2AuP_2Se_6$ at −120 °C: a = 11.961(2) Å, b = 10.069(2) Å, c = 32.137(3) Å, β = 91.37(1)°, V = 3869(2) Å^3, Z = 12, D_c = 4.653 g cm^{-3}, space group $P2_1/n$ (No. 14), μ(Mo Kα) = 356.36 cm^{-1}, $2\theta_{max}$ = 45.1°, octants collected $0 < h < 14$, $0 < k < 12$, $-38 < l < 38$; number of total data collected 5724; number of unique data 5419 (R_{int} = 0.024); number of data with $F_o^2 > 3\sigma(F_o^2)$ 3524; number of variables 289. An empirical absorption correction based on ψ scans was applied to the data, followed by a DIFABS[12c] correction to the isotropically refined data. All atoms were refined anisotropically. Final R/R_w= 0.040/0.048.

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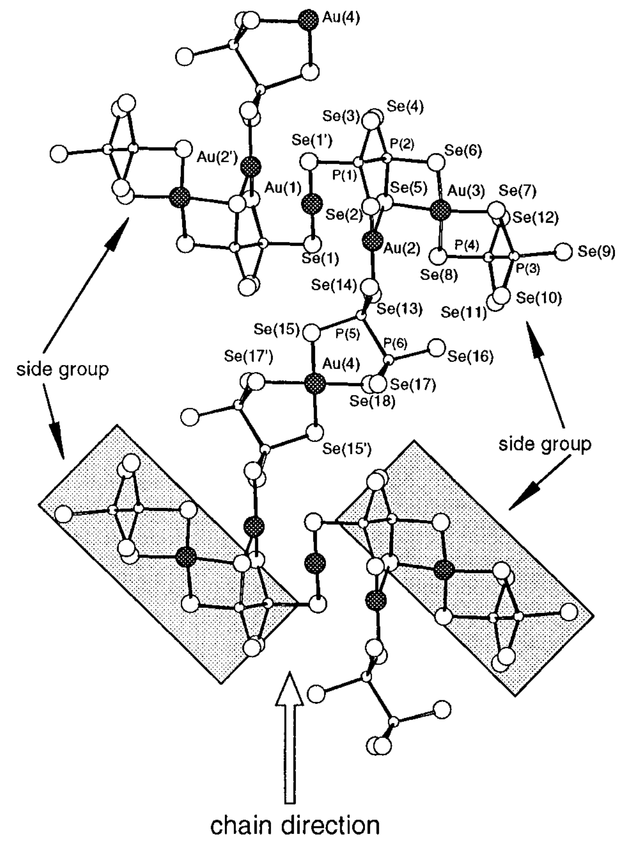

Figure 2. View showing a section of the chain in $A_2AuP_2Se_6$ with labeling. Selected distances (Å): Au(1)−Se(1) 2.402(2), Au(2)−Se(2) 2.494(3), Au(2)−Se(5) 2.680(2), Au(2)−Se(13) 2.423(3), Au(3)−Se(5) 2.489(2), Au(3)−Se(6) 2.479(3), Au(3)−Se(7) 2.455(2), Au(3)−Se(8) 2.457(3), Au(4)−Se(15) 2.461(2), Au(4)−Se(17) 2.492(2), Se(1)−P(1) 2.220(6), Se(2)−P(1) 2.197(6), Se(3)−P(1) 2.132(6), similar distances for the remainder of P−Se bonds, P(1)−P(2) 2.267(8), P(3)−P(4) 2.256(8), P(5)−P(6) 2.219(8). Selected angles (deg): Se(1)−Au(1)−Se(1) 180.0(0), Se(2)−Au(2)−Se(5) 106.78(8), Se(2)−Au(2)−Se(13) 137.16(8), Se(5)−Au(2)−Se(13) 114.69(8), Se(5)−Au(3)−Se(6) 86.18(7), Se(5)−Au(3)−Se(8) 86.60(7), Se(6)−Au(3)−Se(7) 87.14(7), Se(7)−Au(3)−Se(8) 100.07(8), Se(15)−Au(4)−Se(17) 98.88(7), Se(15)−Au(4)−Se(17′) 81.12(7).

2). In addition, the packing of these chains creates channels running parallel to the *b* axis where the cations are residing (Figure 1). The Au−Se distance for Au(1)−Se(1) is 2.402(2) Å, which compares very well with those found in $KAuSe_5$[9] and $CsAuSe_3$,[10] all featuring linearly coordinated Au(I). Selected distances and angles are given in the caption to Figure 2. Au−Se distances for the square planar Au(3) and Au(4) average at 2.47(2) Å, and they are also in excellent agreement with those found in K_3AuSe_{13},[9] Na_3AuSe_8,[10] and $AAuSe_2$[10] (A = Na, K), all featuring square planar Au(III). The distorted trigonal geometry of Au(2) involves two similar distances [Se(2) 2.494(3) Å, Se(13) 2.423(3) Å] and a longer one [Se(5) 2.680(2) Å]. The phosphorus−selenium distances range from 2.120(6) to 2.258(6) Å, with the noncoordinated selenium atoms (e.g. Se(3), Se(4), Se(9), etc.) displaying the shorter ones. The phosphorus−phosphorus bonds range from 2.219(8) Å for P(5)−P(6) to 2.267(8) Å for P(1)−P(2). There are two coordination environments for the rubidium cations. One out of the six crystallographically independent cations is eight-coordinate [Rb−Se mean = 3.6(1) Å] and five are nine-coordinate [Rb−Se mean = 3.7(1) Å].

The solid-state UV/vis diffuse reflectance spectra of $A_2AuP_2Se_6$ show sharp optical gaps consistent with semiconductors in the range 1.1−1.2 eV. The infrared spectra of both compounds display absorptions at similar energies at ~504, ~490, ~422, ~411, ~304, ~294, ~227, and ~214 cm^{-1}. Whereas similar absorptions have been observed for other compounds with the $[P_2Se_6]^{4-}$ group,[1] this is the first time that a splitting of the peaks can be observed which corresponds to the differently coordinated $[P_2Se_6]^{4-}$ groups. In particular, the 504, 490 cm^{-1} vibrations which can be attributed to PSe_3 stretching modes[1] have counterparts at 422, 411 cm^{-1} as well. Similarly, the medium absorbance at ~300 cm^{-1} which was ascribed to an out-of-phase PSe_3 mode[1] has been split to one at 304 cm^{-1} and one at 294 cm^{-1}. A tentative assignment of the lower energy peaks 422, 411, 294 cm^{-1} can be made to the first $[P_2Se_6]^{4-}$ group that connects Au(1), Au(2), and Au(3), since its higher connectivity would reduce the energy of the PSe_3 stretching modes. The higher energy absorbances should contain the stretching modes for the remaining two kinds of $[P_2Se_6]^{4-}$ which possess lower connectivity.

Differential thermal analysis (DTA) shows that $K_2AuP_2Se_6$ and $Rb_2AuP_2Se_6$ melt at 457 and 474 °C, respectively. An interesting feature of the DTA is that the compounds give two exothermic peaks upon cooling. For example, $K_2AuP_2Se_6$ gives two exothermic peaks at 451 and 426 °C. Upon two more heating and cooling cycles, the peaks remained unchanged and examination of the ingot with X-ray powder diffraction and EDS analysis did not indicate any decomposition. Further thermal analysis (DTA, DSC) of the $Au/P_2Se_5/A_2Se/Se$ system is under way to investigate the presence of a phase transition.[11]

In summary, the first selenophosphate gold compounds have been prepared in molten polyselenophosphate $A_x[P_ySe_z]$ fluxes. Other related compounds from the gold system include $A_2Au_2P_2Se_6$ and $A_3AuP_2Se_8$, and they feature the linearly coordinated Au(I).[11]

$A_2AuP_2Se_6$ is the first compound known to stabilize in its structure all possible coordination environments for gold. Its unexpected structural characteristics provide a stimulating example of the rich chemistry that becomes accessible with the use of the flux method in various metal systems.

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Supporting Information Available: Tables of crystallographic details, fractional atomic coordinates of all atoms, anisotropic and isotropic thermal parameters of all atoms, and interatomic distances and angles for $Rb_2AuP_2Se_6$, calculated and observed X-ray powder data for $Rb_2AuP_2Se_6$, and observed X-ray powder data for $K_2AuP_2Se_6$ (14 pages). Ordering information is given any current masthead page.

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(8) There is a high-pressure metastable phase of $CsAuI_3$ which, at 6.8 GPa and at 167 °C, was reported to have a cubic perovskite structure. This would imply that the Au^{II} coordination geometry would be octahedral; however, no refinement of the diffraction data (powder XRD data) has been carried out and the possibility of local displacements of the gold centers from the ideal octahedral pockets has not been unambiguously eliminated. The related X-ray isomorphous compound $CsAu_{0.6}Br_{2.6}$, also studied with powder diffraction, has too many vacancies to allow one to unequivocally establish the true local coordination of gold. A full single-crystal crystallographic refinement is needed to establish the gold coordination in these materials. (a) Kojima, N.; Hasegawa, M.; Kitagawa, T.; Shimomura, O. *J. Am. Chem. Soc.* **1994**, *116*, 11368−11374. (b) Kitagawa, T.; Kojima, N.; Matsushita, N.; Ban, T.; Tsujikawa, I. *J. Chem. Soc., Dalton Trans.* **1991**, 3115−3119.

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