$(Ph_4P)_4[Pd_7As_{10}S_{22}]$: A Sulfosalt with a Large Cluster Anion Whose Structure Resembles a Gondola

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The hydro(solvento)thermal technique was demonstrated to generate a useful set of experimental conditions which can lead to novel quaternary chalcoarsenate compounds.[1−3] The hydro(solvento)thermal behavior of the $R_4E^+/M^{n+}/[AsQ_3]^{3-}$ (E = R, N; R = Ph, alkyl; M = metal; Q = S, Se) systems lead to the synthesis of a number of unusual compounds such as $(Ph_4P)_2[InAs_3S_7]$,[4] $(Me_4N)_2Rb[BiAs_6S_{12}]$,[4] $(Ph_4P)_2[Hg_2As_4S_9]$,[5a] $(Me_4N)[HgAs_3S_6]$,[5a] $(Me_4N)[HgAsSe_3]$,[5b] $(Et_4N)[HgAsSe_3]$,[5b] $(Ph_4P)_2[Hg_2As_4Se_{11}]$,[5b] $(Ph_4P)_2[Pt(As_3S_5)_2]$,[6] $(Ph_4P)_2K[Pt(AsS_4)_3]\cdot 1.5H_2O$,[6] β-Ag_3AsSe_3,[7] $(Me_3NH)[Ag_3As_2Se_5]$,[7] $K_5Ag_2As_3Se_9$,[7] $KAg_3As_2Se_5$,[7] $(Ph_4P)_2[Ni_2As_4S_8]$,[8] $(Me_4N)_2[Mo_2O_2As_2S_7]$,[8] and $(Et_4N)_2[Mo_2O_2As_2Se_7]$.[8] The most characteristic feature of these compounds is the presence of higher nuclearity $[As_xQ_y]^{n-}$ units formed by the condensation reactions of the fundamental building unit $[AsQ_3]^{3-}$. The type and identity of the $[As_xQ_y]^{n-}$ anions, found in the isolated compounds, depends on the particular counterion present, on the metal size and coordination preference and on the solvent used. Extension of this chemistry to Pd looked appealing because no quaternary chalcoarsenate compounds with this metal have been reported. Furthermore, Pd has given rise to some surprising results under hydro(solvento)thermal conditions.[9] The great lability of the $[AsQ_3]^{3-}$ anion and its catenation properties to form higher nuclearity $[As_xQ_y]^{n-}$ units raises interesting prospects for similar chemistry in this system. Here we report the synthesis, structural characterization, and optical properties of a new molecular palladium thioarsenate compound $(Ph_4P)_4[Pd_7As_{10}S_{22}]$ whose unusual anionic structure resembles a gondola. This "gondola" is held together by both Pd−S and Pd−As bonds.

$(Ph_4P)_4[Pd_7As_{10}S_{22}]$ is air-stable and soluble in polar organic solvents, such as CH_3CN and DMF, forming an orange solution.[10] The anion in $(Ph_4P)_4[Pd_7As_{10}S_{22}]$ contains two different thioarsenate units, $[As_2S_5]^{4-}$ and $[As_3S_6]^{5-}$, linked to Pd atoms, and it is curiously shaped like a gondola, see Figure 1.[11] As a result, $(Ph_4P)_4[Pd_7(As_2S_5)_2(As_3S_6)_2]$ is a more descriptive formula. The $[As_3S_6]^{5-}$ unit is unprecedented and can be viewed as a two-electron reduction product of the linear $[As_3S_7]^{5-}$ unit,[4] see Scheme 1. The nature of the reducing agent is unclear but it could be sacrificial $[AsS_3]^{3-}$ anions which exist in excess in solution.

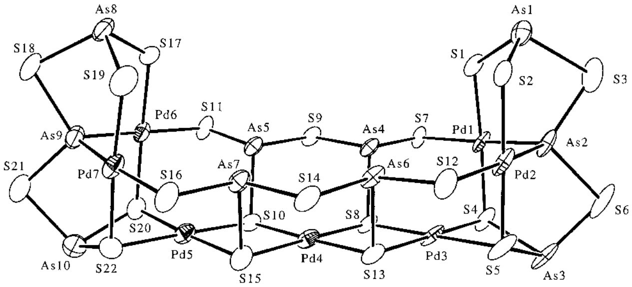
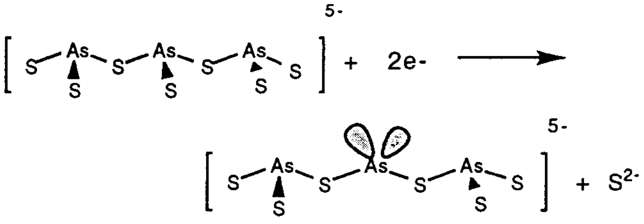


Figure 1. Structure of the $[Pd_7As_{10}S_{22}]^{4-}$ anion with atomic labeling.

Scheme 1



We can assign the formal oxidation state of the terminal As atoms in $[As_3S_6]^{5-}$ as 3+, while the bridging As atom (i.e. As2 and As9) is assigned an oxidation state of 1+. The As−S bond distances range from 2.256(8) to 2.326(7) Å. The As−Pd bond distances are essentially equal at 2.376(3) Å. The $[As_3S_6]^{5-}$ units

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(1) (a) Liao, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1992**, *31*, 431−439. (b) Liao, L. H.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 7400−7402. (c) Huang, S.-P.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 5477−5478. (d) Kim, K.-W.; Kanatzidis, M. G. *J. Am Chem Soc.*, **1992**, *114*, 4878−4883.

(2) (a) Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1988**, *562*, 23−30. (b) Sheldrick, W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 98−104. (c) Sheldrick, W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 105−110. (d) Sheldrick, W. S.; Wachhold, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 206−224.

(3) (a) Wood, P. T.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1993**, *32*, 129−130. (b) Wood, P. T.; Pennington, W. T.; Kolis, J. W. *J. Chem. Soc. Chem. Commun.* **1993**, *25*, 235−236. (c) Drake, G. W.; Kolis, J. W. *Coord. Chem. Rev.* **1994**, *137*, 131−178.

(4) Chou, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1994**, *33*, 1001−1002.

(5) Chou, J.-H.; Kanatzidis, M. G. *Chem. of Mater.* **1995**, *7*, 5−8.

(6) Chou, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1994**, *33*, 5372−5373.

(7) Kanatzidis, M. G.; Chou, J.-H. *J. Solid State Chem.* **1996**, in press.

(8) Chou, J.-H.; Hanko, J. A.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 4−9.

(9) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 5606−5607.

(10) (a) $(Ph_4P)_4[Pd_7As_{10}S_{22}]$: A mixture of $PdCl_2$ (0.044 g; 0.25 mmol), K_3AsS_3 (0.072 g; 0.25 mmol), Ph_4PBr (0.628 g; 1.5 mmol), and 0.3 mL of methanol was sealed under vacuum and kept at 110° C for 3 days. The large red platelike crystals formed were isolated in methanol and washed with ether (yield = 75% based on $PdCl_2$). A semiquantitative elemental analysis of the red crystals using a scanning electron microscope/energy dispersive analysis gave an average composition of $P_1Pd_{1.9}As_2S_{5.6}$. The purity of the material was also confirmed with a comparison of the calculated and observed X-ray powder diffraction data. (b) The optical spectrum of $(Ph_4P)_4[Pd_7As_{10}S_{22}]$ shows a sharp optical transition with an onset of 623 nm. The Raman spectrum of $(Ph_4P)_4[Pd_7As_{10}S_{22}]$ shows three absorptions. One at 251 cm^{-1} (tentatively assigned to an As−S vibration), a second absorption at 186 cm^{-1} (assigned to Pd−S vibrations), and a third at 151 cm^{-1} (perhaps As−Pd stretching).

(11) (a) A Siemens SMART Platform CCD diffractometer was used to collect data from a crystal of 0.10 × 0.10 × 0.01 mm dimensions with a 20 s/frame collection speed and Mo Kα ($\lambda = 0.710\ 73$ Å) radiation. Lorentz polarization effects correction and an empirical absorption correction[11c] were applied to the data. (b) The crystal was solved by direct methods and refined using the SHELXTL-5 package of crystallographic programs; SHELXTL-5 refines on F^2. Crystal data at −148 °C: $a = 28.908(1)$ Å; $b = 18.3744(8)$ Å; $c = 24.487(1)$ Å; $b = 108.496(1)°$; $V = 12335.2(9)$ Å^3; $Z = 4$; $D_c = 1.90$ g/cm^3; space group $P2_1/c$ (No. 14); μ(Mo Kα) 4.125 cm^{-1}; index ranges $-37 \leq h \leq 25$, $-24 \leq k \leq 22$, $-32 \leq l \leq 32$; total no. of data, 61 114; unique no. of data, 27 145 ($R_{int} = 0.353$); no. of data with $F_o^2 > 2\sigma(F_o^2)$, 27 145; no. of variables, 756; final $R/wR^2 = 0.1080/0.2133$; GOF = 0.782. (c) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38. (d) Sheldrick, G. M. *SHELXTL Version 5.03*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.

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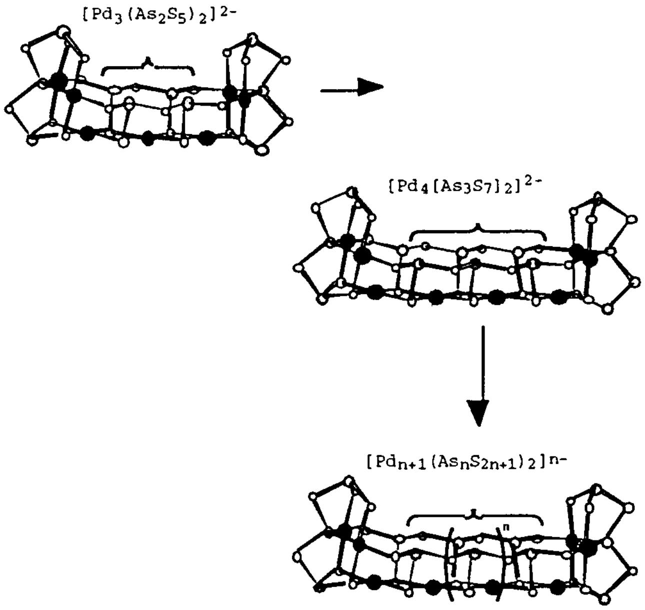
Table 1. Selected Bond Distances (Å) for $(Ph_4P)_4[Pd_7As_{10}S_{22}]$

Pd(1)−S(1)	2.323(7)	As(1)−S(1)	2.278(7)
Pd(1)−As(2)	2.376(3)	As(1)−S(2)	2.254(7)
Pd(1)−S(4)	2.392(7)	As(1)−S(3)	2.331(8)
Pd(1)−S(12)	2.427(6)		
		As(2)−S(3)	2.259(8)
Pd(2)−S(2)	2.347(7)	As(2)−S(4)	2.319(7)
Pd(2)−As(2)	2.372(3)		
Pd(2)−S(5)	2.388(7)	As(3)−S(5)	2.315(7)
Pd(2)−S(12)	2.427(7)	As(3)−S(4)	2.333(8)
		As(3)−S(6)	2.345(9)
Pd(3)−S(13)	2.364(7)		
Pd(3)−S(5)	2.368(7)	As(4)−S(7)	2.226(6)
Pd(3)−S(8)	2.364(6)	As(4)−S(9)	2.307(7)
Pd(3)−S(4)	2.406(7)	As(4)−S(8)	2.337(7)
Pd(4)−S(8)	2.364(6)	As(5)−S(10)	2.347(7)
Pd(4)−S(15)	2.380(7)	As(5)−S(9)	2.310(7)
Pd(4)−S(13)	2.380(7)	As(5)−S(11)	2.229(7)
Pd(4)−S(10)	2.390(7)		
		As(6)−S(12)	2.226(7)
Pd(5)−S(10)	2.374(7)	As(6)−S(14)	2.316(7)
Pd(5)−S(15)	2.400(7)	As(6)−S(13)	2.331(7)
Pd(5)−S(20)	2.400(7)		
Pd(5)−S(22)	2.405(7)	As(7)−S(15)	2.365(7)
		As(7)−S(14)	2.337(7)
Pd(6)−S(17)	2.350(7)	As(7)−S(16)	2.223(7)
Pd(6)−As(9)	2.378(3)		
Pd(6)−S(20)	2.389(7)	As(8)−S(17)	2.257(7)
Pd(6)−S(11)	2.411(7)	As(8)−S(18)	2.313(8)
		As(8)−S(19)	2.296(8)
Pd(7)−S(19)	2.317(8)		
Pd(7)−As(9)	2.376(4)	As(9)−S(18)	2.275(8)
Pd(7)−S(22)	2.387(7)	As(9)−S(21)	2.294(8)
Pd(7)−S(16)	2.437(7)	As(10)−S(20)	2.312(8)
		As(10)−S(21)	2.283(8)
		As(10)−S(22)	2.306(8)

are asymmetrically connected to four Pd atoms forming the bow and stern of the gondola. The two sulfur atoms associated with the upper As atoms (i.e. As1 and As8) are bound directly to Pd atoms, while the two sulfides from the lower As atoms (i.e. As3 and As10) bridge these Pd atoms and the Pd atoms on the floor of the gondola. The $\{Pd_2[As(AsS_3)_2]\}^-$ fragment is reminiscent of the molecular species $[Ag_2Te(TeS_3)_2]^{2-}$,[12] where the Ag is replaced with Pd and the $[Te(TeS_3)_2]^{4-}$ fragment is replaced by the isoelectronic $[As(AsS_3)_2]^{5-}$ unit. The two $\{Pd_2[As(AsS_3)_2]\}^-$ fragments are connected together by a $[Pd_3(As_2S_5)_2]^{2-}$ fragment. The latter forms the walls and the floor of the gondola. The Pd atoms have a slightly distorted square-planar coordination with Pd−S bond distances ranging from 2.363(7)−2.405(7) Å, and S−Pd−S angles ranging from 83.4(2) to 95.9(2)°. Selected bond distances are given in Table 1.

Scheme 2



It is useful to regard the gondola as two $\{Pd_2[As(AsS_3)_2]\}^-$ fragments connected together by a $[Pd_3(As_2S_5)_2]^{2-}$ unit. The $[Pd_3(As_2S_5)_2]^{2-}$ unit can be thought of as a variable "spacer" between the two $\{Pd_2[As(AsS_3)_2]\}^-$ fragments. Since several higher nuclearity thioarsenate units are known,[1−8] it may be possible to build longer gondolas through the formation of longer $[Pd_x(As_yS_z)_2]^{n-}$ spacers. The simplest example is to replace the two $[As_2S_5]^{4-}$ units with two $[As_3S_7]^{5-}$ units and an additional Pd atom. The complete extension of this is the insertion of an oligomeric spacer of the general formula $[Pd_{(n+1)}(As_nS_{(2n+1)})]^{n-}$, see Scheme 2. Therefore, the compound reported here could be a member of a putative homologous family of gondolas of the general formula $\{[Pd_2(As_2S_6)]_2[Pd_{(n+1)}(As_nS_{(2n+1)})_2]\}^{-(n+2)}$. Access to other members may be possible with further exploration of the hydro(solvento)thermal chemistry of the $R_4E^+/Pd/[AsQ_3]^{3-}$ system.

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Supporting Information Available: Tables of the fractional atomic coordinates, bond distances, bond angles, and anisotropic and isotropic thermal parameters of all non-hydrogen atoms (10 pages). Ordering information is given on any current masthead page.

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[12] Chung, D. Y.; Huang, S.-P.; Kim, K.-W. *Inorg. Chem.* **1995**, *34*, 4292−4293.