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Charged Molecular Alloys: Synthesis and Characterization of the Binary Anions $Pd_7As_{16}^{4-}$ and $Pd_2As_{14}^{4-}$

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The relationship between the fullerenes and the E_9^{4-} clusters (E = Si, Ge, Sn, Pb) has fueled a resurgence in the chemistry of Zintl anions and their oxidatively coupled derivatives.[1,2] The use of these materials for the development of novel nanomaterials has also been noted.[1,2] For similar reasons, we have been interested in the synthesis of charged, ligand-free homoleptic binary anions derived from ligand-stabilized metalated Zintl anions, such as the $[As_7PtH(PPh_3)]^{2-}$ and $[Sb_7Ni_3(CO)_3]^{3-}$ complexes.[3,4] Unfortunately, displacement of the stabilizing ancillary ligands from these preformed complexes has proven to be difficult. By contrast, the direct synthesis of ligand-free binary anions from weakly coordinated transition metal precursors is emerging as a more successful synthetic approach.[5−7]

Transition metal/main group binary anions are known for the halides (e.g. $PdCl_6^{2-}$) and the chalcogenides (e.g. MoS_4^{2-}).[8] However, there are no examples of transition metal binary anions of group 14 or 15 elements aside from the $NbAs_8^{3-}$ and $MoAs_8^{2-}$ ions.[5,9] Herein we report two new unusual complexes, $Pd_7As_{16}^{4-}$ and $Pd_2As_{14}^{4-}$, that, together with the ME_8^{n-} ions, constitute a new class of binary cluster anions that can be viewed as charged molecular alloys.

Ethylenediamine (en) solutions of As_7^{3-} (**1**) react with toluene (tol) solutions of $Pd(PCy_3)_2$, where Cy = cyclohexyl, in the presence of 2,2,2-crypt to give $Pd_2As_{14}^{4-}$ (**2**) in ca. 20% crystalline yield as the $[K(2,2,2\text{-crypt})]^+$ salt (eq 1).[10] The $Pd_2As_{14}^{4-}$ product results from a net two-electron oxidation of the Pd/As precursors, which is facilitated by a two-electron reduction of en solvent molecules and subsequent H_2 elimination. The formation of H_2 gas in eq 1

$$2Pd(PCy_3)_2 + 2As_7^{3-} + 2en \rightarrow \underset{\mathbf{2}}{Pd_2As_{14}^{4-}} + 4PCy_3 + 2NH_2(CH_2)_2NH^{1-} + H_2 \quad (1)$$

was verified by a hydrogen trapping experiment involving the hydrogenation of *trans*-stilbene in the presence of a Pd catalyst (eq 2).[6,10] The head gases from eq 1 were used as the H_2 source in

$$PhCH{=}CHPh + H_2 \xrightarrow{[Pd]/C} PhCH_2CH_2Ph \quad (2)$$

eq 2. Similar solvent activation processes were observed[3,6] in the formation of the related Pt complexes $[As_7PtH(PPh_3)]^{2-}$ and $[Sn_9Pt_2(PPh_3)]^{2-}$. Deuterium-labeling experiments in the previous studies confirmed that the hydride ligands and H_2 gas originated from the activation of coordinating solvent molecules (en, dmf, dmso). The binary anion **2** has been characterized by semiquantitative EDX analysis, electrospray mass spectrometry (ESI-MS), and single-crystal X-ray diffraction.[11] The ESI-mass spectrum of **2** (dmf solution, negative ion mode) shows peaks for the $[K(2,2,2\text{-crypt})\text{-}H_2Pd_2As_{14}]^{1-}$ ion (strong) and the $HPd_2As_{14}^{-1}$ ion (weak) along with peaks for various degradation products. We also observe a $Pd_2As_9^{1-}$ ion of unknown structure (see Supporting Information). It is common[2] to observe oxidized and/or protonated transition metal Zintl ions by ESI-MS and, in fact, we have yet to observe a fully charged molecular ion to date. It is also common to observe various alkali-coordinated species (i.e. ion pairs); however, the spectrum of **2** represents the first example of a $[K(2,2,2\text{-crypt})]^+$ ion pair in this chemistry.

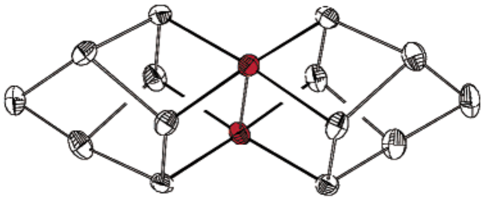
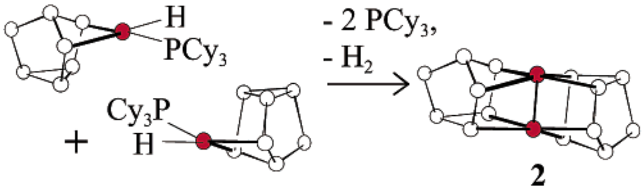


Figure 1. ORTEP drawing of the $Pd_2As_{14}^{4-}$ ion. Pd atoms are in red.

Scheme 1



The structure of **2** (Figure 1) can be viewed as two norbornadiene-like As_7^{5-} groups bound to a Pd_2^{6+} dimetal center in a μ,η^2,η^2 fashion with overall D_{2h} point symmetry. The formally Pd(III) ions are in distorted square planar coordination environments and are linked by an axial Pd−Pd bond of 2.7144(6) Å. Metal−metal bond formation is accomplished through overlap of the singly occupied d_{z^2} orbitals on each Pd center. Dinuclear Pt(III) complexes with Pt−Pt bonds are common[12] whereas Pd(III) dimers are not. The Pd−As bond distances average 2.477(5) Å and are consistent with expectations based on related $Pt{-}As_7$ systems[3] and the differences in Pd/Pt covalent radii. The norbornadiene-like As_7 units have As−As distances in the range 2.3616(7)−2.4455(7) Å, which are similar to those in the $[As_7M(CO)_3]^{3-}$ ions (M = Cr, Mo, W).[13] The As_7 units in **2** differ from the nortricyclane-like anion **1** and the As_7 fragment in $[As_7PtH(PPh_3)]^{2-}$ (**3**).[3] However, it is quite likely that the Pd analogue of **3** is initially formed in eq 1 and is subsequently coupled in a redox process to form **2** (see Scheme 1). The H_2 trapping experiments and observed phosphine elimination are consistent with this proposal but we have not identified any intermediates to date.

In addition to complex **2**, eq 1 chemistry yields low but reproducible amounts of a second cluster, $Pd_7As_{16}^{4-}$ (**4**), as the $[K(2,2,2\text{-crypt})]^+$ salt. The complex has been characterized by ESI-

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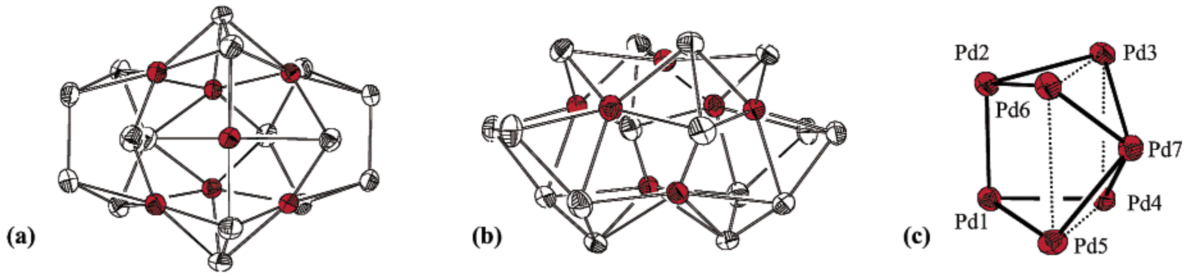

Figure 2. (a, b) Two views of the $Pd_7As_{16}^{4-}$ ion. Pd−Pd bonds are omitted for clarity. (c) The Pd_7 core of the $Pd_7As_{16}^{4-}$ ion. Pd atoms are in red.

MS, semiquantitative EDX analysis, and single-crystal X-ray diffraction.[11] The crystal is triclinic with two independent and statistically identical $Pd_7As_{16}^{4-}$ ions, eight $[K(2,2,2\text{-crypt})]^+$ ions, and 3.5 en solvates in the asymmetric unit. The structure of **4** (Figure 2) contains overall C_{2v} point symmetry with a highly distorted capped trigonal prismatic Pd_7 core (Figure 2c), 2 As_5 rings, 2 As_2 units, and 2 As atoms. The distorted capped trigonal prismatic Pd_7 unit can also be viewed as two cyclopentane-like rings fused at a common edge (Pd1−Pd2) and a common vertex (Pd7). For electron bookkeeping, charges can be assigned as follows: 2 As_5^{1-}, 2 As_2^{2-}, and 2 As^{3-} with 6 trigonal prismatic Pd(I) ions and a square-planar Pd(II) ion, Pd7, that caps one face of the trigonal prism. The Pd(I) ions exist in two different five-coordinate geometries, namely $Pd(\eta^2\text{-}As_5)_2(\eta^1\text{-}As_2)$ for Pd1 and Pd2, and $Pd(\eta^2\text{-}As_5)(\eta^2\text{-}As_2)(As)$ for Pd3−Pd6. The square-planar coordination about Pd7 is defined by *trans*-$Pd(As)_2(\eta^1\text{-}As_2)_2$.

The mass spectrum of the As_7^{3-} precursor solution shows the presence of both As_5^{1-} and As_2^{2-} ions along with **1**, which suggests that **4** forms from the polyarsenide species available in solution and does not result from a successive degradation of **2** or related complexes. Although the arsenic fragments have all been observed individually in other coordination complexes,[14] the structure of **4** is unprecedented in that it is a binary ion unsupported by organic ligands.

The Pd_7 core differs from other Pd_7 clusters[15] and the related Pd nanoclusters with close packed arrays of Pd atoms.[16] The Pd−Pd separations fall in two ranges: 2.800(1)−2.907(1) Å (Figure 2c, solid lines) and 3.564(1)−3.714(1) Å (Figure 2c, dashed lines). The latter are nonbonding separations whereas the former are slightly longer than those of related organometallic nanoclusters[16] and *ccp* Pd metal (2.75 Å).[17] The Pd−As bonds vary from 2.435(1) Å to 2.651(1) Å whereas the As−As bonds are in the range 2.410(1)−2.495(1) Å. Four long secondary bonds between the As^{3-} ions and the As_5^{1-} rings are observed with contacts in the range 2.752(1)−2.833(1) Å.

The two complexes described herein are rare examples of organic-free homoleptic binary anions containing group 15 elements and represent an emerging class of charged "molecular alloys". The use of these anions for the synthesis of nanosized intermetallics has shown promise in the Sn−Pt systems[6] and may be equally fruitful in the present case. Oxidation studies are currently in progress.

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Supporting Information Available: Crystallographic data (CIF) and ESI-MS data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) In vial 1, K_3As_7 (50.0 mg, 0.0779 mmol) and 2,2,2-crypt (57.3 mg, 0.156 mmol) were dissolved in en (∼2 mL) and stirred for 5 min, yielding a dark red solution. In vial 2, $Pd(PCy_3)_2$ (52.0 mg, 0.0779 mmol) was dissolved in tol (∼1 mL) yielding a pale yellow solution. The solution from vial 2 was added dropwise to vial 1 and the mixture was stirred for 5 h, yielding a dark reddish-brown solution. The solution was then filtered through tightly packed glass wool. The filtered solution was refluxed for 15 min and filtered again. After 1−4 days, black parallelepiped crystals of $[K(\text{crypt})]_4\mathbf{2}\cdot 5\text{en}$ and black plate-like crystals of $[K(\text{crypt})]_8\mathbf{4}_2\cdot 3.5\text{en}$ precipitated. Yield: ∼25 mg (∼20%) of mixed crystals. Optical inspection and MS analysis suggest an ∼10:1 ratio of **2**:**4**. For $[K(2,2,2\text{-crypt})]_4[Pd_2As_{14}]\cdot 5\text{en}$, EDX As:Pd:K = 7.10:1.00:1.96; MS (ESI) *m/z* 1679 $[K(2,2,2\text{-crypt})Pd_2As_{14}]^{-1}$. For $[K(2,2,2\text{-crypt})]_8[Pd_7As_{16}]_2\cdot 3.5\text{en}$, EDX As:Pd:K = 2.37:1.00:4.00; MS (ESI) *m/z* 1985 $[KAs_{16}Pd_7]^-$. Hydrogenation: A Pd/C catalyst (10%, Aldrich) was suspended in a hexane solution of *trans*-stilbene in a closed container in contact with the head gases from eq 1.
(11) Crystal data for $[K(2,2,2\text{-crypt})]_4[Pd_2As_{14}]$◊5en: A black parallelpiped crystal 0.573 × 0.396 × 0.277 mm^3 was analyzed using a Bruker SMART1000 single-crystal CCD-diffractometer operating at 193 K. Data were corrected for absorption (SADABS) and L−P effects and the structure solved and refined (against F^2) using the SHELXTL software package. Monoclinic, space group $C2/c$, $a = 15.9132(10)$ Å, $b = 23.7330(14)$ Å, $c = 34.141(2)$ Å; $\beta = 90.8170(10)°$, $V = 12892.8(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.661$ g cm^{-1}, $1.54° < \theta < 27.5°$, Mo Kα radiation, μ(Mo Kα) = 4.039 mm^{-1}, 14810 unique reflections for 656 parameters. GOF (F^2) = 1.051, $R1 = 0.0431$, $wR2 = 0.1051$ for $I > 2\sigma(I)$ [10255 data] and $R1 = 0.0753$, $wR2 = 0.1147$ for all data. For $[K(2,2,2\text{-crypt})]_8[Pd_7As_{16}]_2\cdot 3.5\text{en}$: A black plate of dimensions 0.50 × 0.20 × 0.02 mm^3 was analyzed and the data processed as described above. Triclinic, space group $P1$, $a = 17.2784(9)$ Å, $b = 27.2637(15)$ Å, $c = 28.9377(16)$ Å; $\alpha = 113.4360(10)°$, $\beta = 99.2890(10)°$, $\gamma = 99.6560(10)°$, $V = 11931.4(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.066$ g cm^{-1}, $0.84° < \theta < 25.00°$, Mo Kα radiation, μ(Mo Kα) = 5.639 mm^{-1}, 42004 unique reflections for 2465 parameters. GOF (F^2) = 1.004, $R1 = 0.0534$, $wR2 = 0.1294$ for $I > 2\sigma(I)$ [23829 data] and $R1 = 0.1180$, $wR2 = 0.1485$ for all data.
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