

Supporting Information

On the Stability of an Unsupported Mercury-Mercury Bond linking Group 15 Zintl Clusters

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EXPERIMENTAL SECTION

All of the reagents used were commercially available. 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Crypt), $\text{Hg}(\text{C}_6\text{H}_5)_2$ and anhydrous ethylenediamine (*en*) (99.5%, purified by redistillation, packed under Ar) were purchased from Aldrich. As powder (-70 mesh, 99.99%), K (99.95%, ampouled under Argon), were purchased from Alfa Aesar. Tetrahydrofuran (THF) were dried by passing through an activated alumina column followed by deoxygenating by passing over a copper catalyst. All glassware (oven dried), reactants, and solvents were stored in a glove box filled with argon.

All manipulations were performed in an argon-filled glove box. The detailed synthetic procedures of the precursors K_3As_7 and compound **1** are summarized below:

Precursor K_3As_7 : The precursors, K_3As_7 was synthesized by mixing of As (~700 mg) with a preheated mixture of K (~120 mg) and *en* (3 ml) in a scintillation vial [K and *en* mixture was stirred at 50 °C for 1 h to dissolve K partially in *en* to produce a blue colored solution]. This mixture was continuously stirred for 30 min at 50 °C followed by the addition of 3 ml of *en* and the mixture was stirred overnight at room temperature. The red suspension was filtered through an Acrodisc premium 25-mm syringe filter with GxF/0.2 μm pores (syringe filter) and the resulting dark red solution was used for further reactions. Note: As and K metals did not completely dissolve.

Compound **1:** In a scintillation vial, 1 ml *en* solution of $\text{Hg}(\text{C}_6\text{H}_5)_2$ (18 mg, 0.05 mmol) was added drop wise to a 2 ml *en* solution of K_3As_7 (33 mg, 0.05 mmol) at room temperature and stirred for 30 min. Crypt (58 mg, 0.15 mmol) was added to this solution and stirred for another 1 h at room temperature. The dark red suspension was filtered through a syringe filter and the resulting dark red solution was layered with THF to allow for crystallization. After 2 days, few dark red rod-like crystals of $[\text{K-Crypt}]_4[\text{Hg}_2(\text{As}_7)_2]$, **1** formed on the wall of the test tube.

Yield was 75%, based on metal and crystals were mono-phasic in nature. The crystals were washed with ethylenediamine and dried in vacuum in glove box and ground finely into the powder form prior to

the measurements. The crystals were air and moisture sensitive. We have taken extra care for all the characterizations.

Initial characterizations were carried out by elemental analysis and energy dispersive X-ray analysis (EDX). Elemental analyses were performed on approximately 10 mg samples (ground crystals) submitted under vacuum. Elemental analysis: calcd (%) for **1**: C 27.22, H 4.65, N 3.59; found: C 27.58, H 5.26, N 3.95. EDAX analysis on many single crystals indicated an Hg: K: As ratio of 1: 2 : 7 for **1** consistent with the single crystal X-ray data.

Single Crystal Structure Determination: X-Ray diffraction data were collected at 120 K on a Bruker APEX diffractometer with a CCD area detector equipped with an X-stream2000 Cryo-system low-temperature device. A suitable crystal was carefully selected under a polarizing microscope and mounted on a loop using N-Paratone oil and quickly placed under the nitrogen flow of the cryo-stream. The X-ray generator was operated at 50 kV and 32 mA using Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. Data were collected with a ω scan width of 0.3°. Total 600, 430 and 235 frames were collected in three different settings of φ (0°, 90°, 180°), keeping the sample-to-detector distance fixed at 5.8 cm and the detector position (2θ) fixed at -25°. Pertinent experimental details of the structure determination of **1** are presented in Table S1.

The data were reduced using SAINTPLUS^{S1} and an empirical absorption correction was applied using the SADABS program.^{S2} The crystal structure was solved by direct methods using SHELXS97 and refined using SHELXL97 present in the SHELXTL V6.14^{S3} package. The last cycles of the refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against F^2 was carried out using the SHELXTL V6.14 package of programs. Crystals of the compound **1** were found to exhibit racemic twinning so that the structure was refined with the application of the twin law [R = (-1 0 0, 0 -1 0, 0 0 -1)] and one BASF parameter. All non-hydrogen atoms were refined anisotropically with DELU instructions to enforce a rigid-bond restraint to the U_{ij}-values of all the bonded atoms. An additional ISOR restraint was applied to the carbon atoms (C11, C17, C33, C54, C69

and C48) to approximate their U_{ij} components to isotropic behavior. All hydrogen atoms were placed in calculated positions during the final step of the refinement process. During refinement, it was also quite evident from an examination of the difference Fourier maps that the asymmetric unit contains highly disordered solvent molecules. However, any attempt to obtain a complete and meaningful model of all the disordered solvent molecules from the residual electron density maps turned out to be unsuccessful. Accordingly, the contribution of the electron density from the solvent-accessible voids (about 2082 \AA^3 per unit cell accommodating a total of 955 electrons) in the crystal structure of **1** was subtracted from the measured structure factors with the BYPASS algorithm, implemented as the SQUEEZE^{S4} option in PLATON.^{S5} CCDC 778125 contain the crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Cyclic Voltammetry: Cyclic voltammetry studies were performed on a SP-150 Bio Logic potentiostat using a Pt-stripe working electrode Pt-stripe counter electrode and Ag/AgCl reference electrode (in 3 M KCl). DMF was used as solvent. 0.1 M lithium tetrafluoroborate was used as supporting electrolyte. Cyclic voltammograms were run at scan rate of 100 mV/s from -1.5 V to 1.0 V at room temperature under Ar atmosphere in a glove box.

Solid State Band Gap Measurements: Diffuse reflectance spectra were collected at room temperature using a Perkin Elmer Lambda 950 UV-Vis-NIR Spectrophotometer, equipped with a Harrick Praying Mantis diffuse reflectance accessory. A photomultiplier tube was used for detection in the 320-860.5 nm range, while a lead sulfide detector was used for the 860.5-2300 nm range. The spectra were collected from 320-2300 nm, with 1.0 nm resolution and integration times of 0.64 s. A dry and finely ground magnesium oxide (MgO) powder was used as a reflectance reference material. Prior to any measurements, all the compounds were finely ground and diluted with MgO to 30% by weight.

Raman Spectroscopy: Compound **1** was subjected to Raman spectral analysis. The Raman microscope system (WITec Alpha SNOM Confocal Raman) consisted of a standard-size light microscope with pinhole diameter of 100 μm , equipped with different objectives coupled to a Raman spectrometer. For this work, a 40x magnification objective, with numerical aperture $NA=0.6$, was used. The spectrometer was equipped with excitation lasers, at 488 nm wavelength. The exposure time of the sample to the laser beam was 5 integration periods of 30 seconds each (30x5), summing 150 seconds total. Measurements were done on powdered samples (grounded single crystals) in sealed glass plates (samples cover with micro cover glass and sealed with high vacuum gel). Control experiment with only glass plates and micro cover glass did not show any Raman active spectra.

Theoretical Calculations: Studies on the cluster solids were carried out using the Vienna *ab initio* stimulation package (VASP) code based on density functional theory (DFT). The projector augmented wave (PAW) pseudopotentials are taken to describe the electron-ion interaction. The generalized gradient approximation (GGA) is used for treating the exchange interactions and correlations. Brillouin zone integrations have been done on Monkhorst-Pack grid k-points, using the tetrahedral method. The kinetic energy cut-off of 350 eV is taken for the plane wave basis. Studies of clusters were done using the ADF DFT code. We used the generalized gradient approximation (GGA) proposed by Perdew, Burke and Enzerhof, with a TZVP basis set, the ZORA (Zeroth Order Regular Approximation) for Relativistic effects was used. The Hirshfeld Charges were calculated to estimate the charge transfer.

REFERENCES

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Table 1. Crystal data and structure refinement parameters for compound **1**.

Compound	Compound 1
Empirical formula	C ₇₂ H ₁₄₄ N ₈ O ₂₄ K ₄ Hg ₂ As ₁₄
Formula weight	3119.44
Crystal system	Orthorhombic
Space group	<i>Pna2(1)</i> (no. 33)
<i>a</i> (Å)	14.029(3)
<i>b</i> (Å)	21.253(5)
<i>c</i> (Å)	43.060(10)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
Volume (Å ³)	12839(5)
Z	4
Size	0.20 × 0.08 × 0.06
ρ_{calc} (g cm ⁻³)	1.610
Absorption coefficient (mm ⁻¹)	6.154
θ range (deg)	0.95 to 25.50
Reflections collected	68784
Unique reflections	23541
Number of parameters	1118
Goodness of fit (S)	0.887
Final R indices [I>2sigma(I)]	R ₁ = 0.0642, wR ₂ = 0.1168

$$R_1 = \frac{\sum \| F_o - |F_c| \|}{\sum |F_o|}; wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$

$$w = 1/[\rho^2(F_o)^2 + (aP)^2 + bP]. P = [\max(F_o, O) + 2(F_c)^2]/3, \text{ where } a = 0.0433$$

and b = 0.0000 for compound **1**.

Table S2. Selected bond distances in compound **1**.

Bond	Distance (Å)
<i>Compound 1</i>	
As(1)-Hg(1)	2.7624(18)
As(2)-Hg(1)	2.7525(18)
As(8)-Hg(2)	2.7496(18)
As(1)-As(3)	2.386(3)
As(1)-As(7)	2.432(2)
As(2)-As(4)	2.385(3)
As(2)-As(7)	2.438(3)
As(3)-As(5)	2.461(3)
As(3)-As(4)	2.488(2)
As(4)-As(5)	2.470(3)
As(4)-As(5)	2.470(3)
As(5)-As(6)	2.355(3)
As(6)-As(7)	2.377(3)
As(8)-As(12)	2.379(3)
As(8)-As(11)	2.444(3)
As(9)-As(10)	2.379(3)
As(9)-As(11)	2.429(2)
As(9)-Hg(2)	2.7540(19)
As(10)-As(13)	2.474(2)
As(10)-As(12)	2.494(2)
As(11)-As(14)	2.383(3)
As(12)-As(13)	2.497(2)
As(13)-As(14)	2.355(3)
Hg(1)-Hg(2)	2.6792(9)

Table S3. Selected bond angles in compound 1.

Angle	Amplitude (°)
<i>Compound 1</i>	
As(3)-As(1)-As(7)	99.94(8)
As(3)-As(1)-Hg(1)	90.48(7)
As(7)-As(1)-Hg(1)	84.00(7)
As(4)-As(2)-As(7)	100.35(8)
As(4)-As(2)-Hg(1)	92.30(7)
As(7)-As(2)-Hg(1)	84.12(7)
As(1)-As(3)-As(5)	104.37(9)
As(1)-As(3)-As(4)	104.07(8)
As(5)-As(3)-As(4)	59.89(6)
As(2)-As(4)-As(5)	104.86(9)
As(2)-As(4)-As(3)	102.11(8)
As(5)-As(4)-As(3)	59.53(6)
As(6)-As(5)-As(3)	107.29(10)
As(6)-As(5)-As(4)	107.75(10)
As(3)-As(5)-As(4)	60.59(7)
As(5)-As(6)-As(7)	98.86(10)
As(6)-As(7)-As(1)	102.68(9)
As(6)-As(7)-As(2)	104.45(9)
As(1)-As(7)-As(2)	94.24(9)
As(12)-As(8)-As(11)	100.62(8)
As(12)-As(8)-Hg(2)	92.43(7)
As(11)-As(8)-Hg(2)	83.69(7)
As(10)-As(9)-As(11)	100.37(8)
As(10)-As(9)-Hg(2)	91.47(7)
As(11)-As(9)-Hg(2)	83.87(7)
As(9)-As(10)-As(13)	104.56(10)
As(9)-As(10)-As(12)	103.60(8)
As(13)-As(10)-As(12)	60.34(6)

As(14)-As(11)-As(9)	102.72(9)
As(14)-As(11)-As(8)	104.11(9)
As(9)-As(11)-As(8)	93.98(9)
As(8)-As(12)-As(10)	102.37(8)
As(8)-As(12)-As(13)	104.66(10)
As(10)-As(12)-As(13)	59.44(6)
As(14)-As(13)-As(10)	106.87(10)
As(14)-As(13)-As(12)	107.39(10)
As(10)-As(13)-As(12)	60.22(7)
As(13)-As(14)-As(11)	99.25(10)

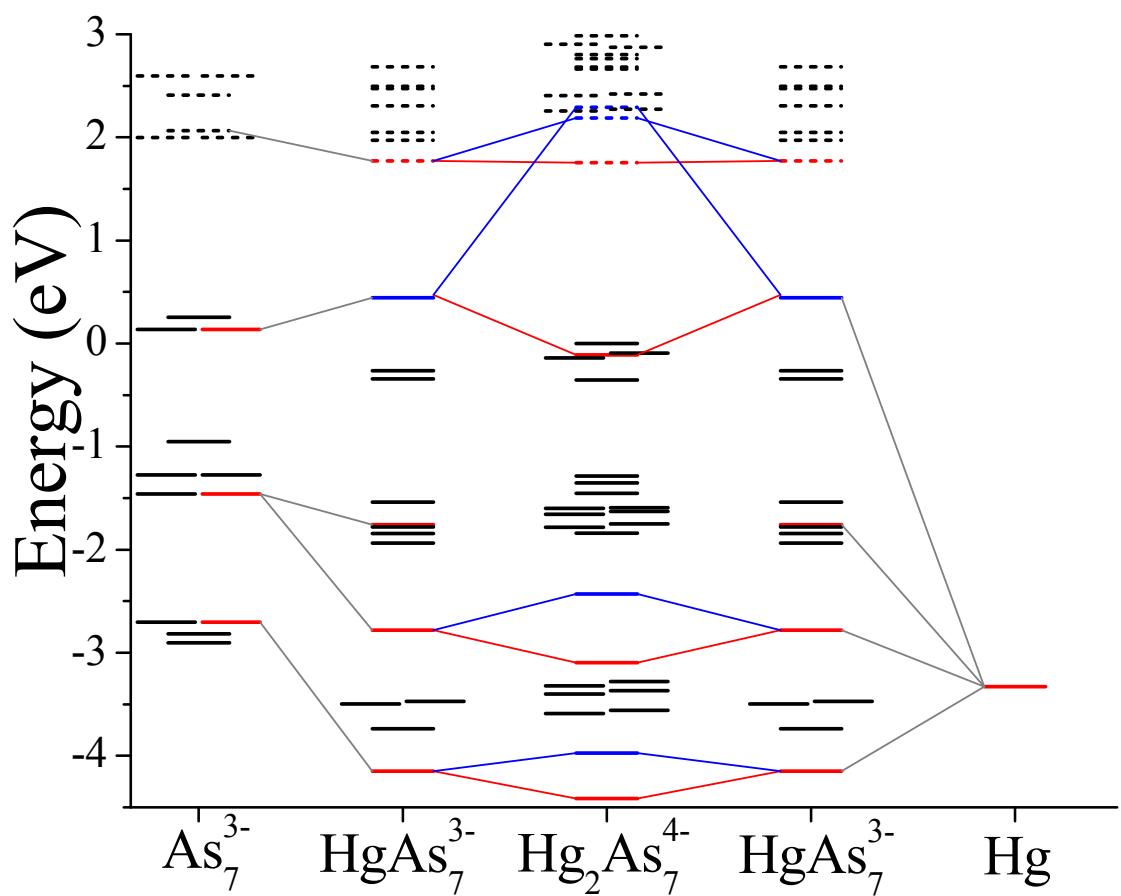


Figure S1. MO diagram for $[\text{Hg}_2(\text{As}_7)_2]^{4-}$. Red states indicate bonding orbitals, blue indicates antibonding orbitals.

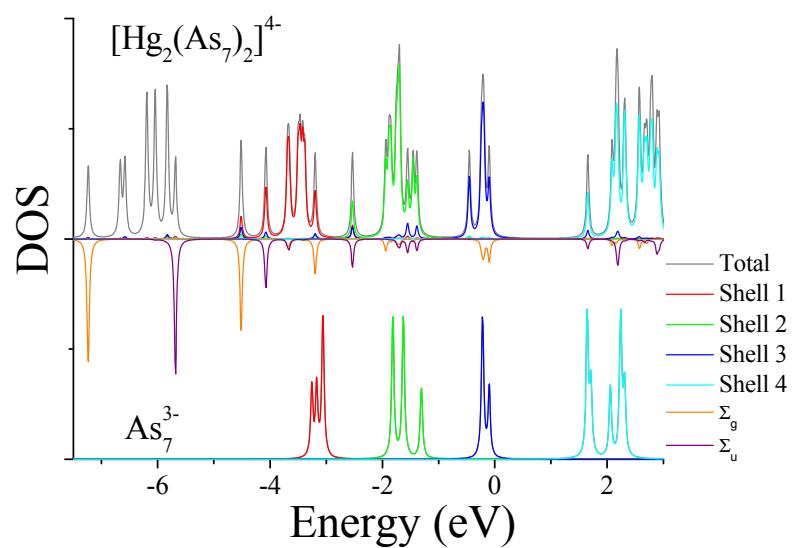


Figure S2. Density of states for As_7^{3-} and $[Hg_2(As_7)_2]^{4-}$. A fragment analysis was used in which the orbitals for As_7^{3-} and Hg_2 in the geometry of the complex are used as a basis set, and these orbitals are projected into the electronic structure of $[Hg_2(As_7)_2]^{4-}$. The DOS on the arsenic clusters are the shell orbitals in As_7^{3-} , and the Σ DOS indicate the orbitals on Hg_2 , and are plotted negatively and doubled.

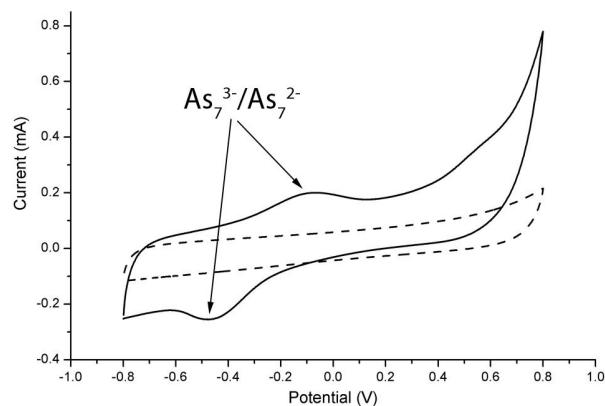


Figure S3. Cyclic voltammogram of 1 mM solution of K_3As_7 in DMF, scanned from -0.8 V to 0.8 V at the scan rate of 100 mV/s. Dashed line represents the blank experiment with DMF and 0.1 M LiBF_4 .