On the stability of an unsupported mercury–mercury bond linking group 15 Zintl clusters
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The dimeric Zintl ion [Hg2(As7)2]4− has been synthesized with high crystalline yield from the reaction of an ethylenediamine solution of the intermetallic Zintl phase K3As7 with diphenyl mercury. Single crystal X-ray diffraction of [K(2,2,2-crypt)]4[Hg2As14], 1 (2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane), reveals that the cluster anion exhibits a Hg–Hg bond and the compound has been further characterized using Raman spectroscopy, cyclic voltammetry and its band gap energy was measured. Theoretical studies provide a microscopic understanding of the bonding in this unusual compound.

Stable molecular compounds featuring a homonuclear metal–metal bond between the group 12 elements have lately been the subject of much discussion in the chemical literature.1,2 For many years, salt-like, ionic species containing [Hg2]2+ units were the only known group 12 compounds with stable metal–metal bonds.3 Seemingly, M–M bonding could be stabilized only in ionic salts, and covalent molecular M(i) compounds of formula RMMR were thought to exist only as short-lived transient species.3–5 In particular, compounds exhibiting Hg–Hg bonds were rare until Apeloig and co-workers reported the first stable, molecular, σ-bonded mercury(i) compound in the form of [Hg2Cl2]2.6 Interestingly, Hg2Cl2 is an ion and in Hg2[Si(SiMe2-SiMe3)3]2 and Hg2[Si(′Me3Si)2],6 the Hg–Hg bond is stabilized through the use of bulky substituents. However, in [As2HgHgAs2]5−, the Hg–Hg bond is sterically accessible and therefore must predominantly be stabilized by the electronic properties of the cluster. Numerous DFT calculations on compounds exhibiting Zn–Zn bonds have demonstrated that the nature of the ligand associated with such species can have a significant effect on the stability of the metal–metal bond.7,9,10

Single crystal structure determination showed that compound 1 contains one [As5HgHgAs5]5− moiety and four [K(2,2,2-crypt)] units in the asymmetric unit (Fig. 1). A crystallographic

Fig. 1 Thermal ellipsoids plot of the crystallographically unique cluster present in compound 1. Anisotropic displacement ellipsoids are shown at 50% probability level. For clarity K-crypt is not shown. For selected bond distances and angles see Tables S2 and S3.†
centre of inversion sits at the centre of the Hg–Hg bond of the crystallographically unique [As2HgHgAs2]4– ion (Fig. 1). The Hg–As bond distances are in the range of 2.749 (2)–2.762(2) Å (av. 2.754 Å) (Table S2†). The Hg–Hg bond distance in compound 1 (2.68 Å) is similar to the Hg–Hg bond in Hg2[Si(SiMe2)3]2 (2.65 Å), but in Hg2I2 (2.67 Å),10 but is significantly longer compared to the oligomeric compounds Hg2F2 (2.508 Å),10 Hg2Cl2 (2.53 Å),10 and Hg2Br2 (2.49 Å).12 and Ar′ HgHgAr′ (2.57 Å).8 This kind of metal–metal bond has been observed in the Au dimer-linked Zintl ion clusters.13 The Au–Au distances are significantly longer (2.90 to 3.11 Å) compared to the Hg–Hg bond distance in compound 1.13 The cluster can be rationalized as a conjuncto-species made up of two As2Hg clusters.

To understand the unexpected formation of the Hg–Hg bond in compound 1, we examined the molecular orbital diagram of [Hg2(As7)2]4–. The free Hg–Hg dimer is a van der Waals molecule;14–16 the valence 6s electrons form a bonding (Fig. 2a) and antibonding (Fig. 2b) pair that results in a bond order of zero. The oxidation of Hg2 to Hg22+ results in a bond order of one and enhanced stability compared to the neutral molecule. In the case of As73–, the 6s orbital of the Hg atom mixes with the HOMO – 1 orbital (Fig. 2c) of the As73– cluster that forms the molecular orbitals shown in Fig. 2e. When the two [HgAs7]3– motifs are brought together, the states split into bonding (Fig. 2g) and antibonding states (Fig. 2j), and the antibonding state becomes unfilled. This results in a net bond order of one for the Hg–Hg bond, and a calculated bonding energy of 1.32 eV. The antibonding orbital is pushed up in energy to become LUMO + 4. The [Hg2(As7)2]4– ion is stabilized through oxidative coupling between the cluster–mercury complex, which pushes up the sigma antibonding orbital to reduce the oxidation state by two. The full molecular orbital diagram and density of states is shown in Fig. S1 and S2.† The formation of the [Hg2(As7)2]4– complex through oxidative coupling is analogous to the stabilization of the [Hg2]2+ dimer through the oxidative coupling of the two “closed electronic shell” species.

The compound 1 is soluble in dimethylformamide (DMF), and this solubility has enabled us to examine the redox chemistry.17 Cyclic voltammetry measurements were carried out on 1 mM DMF solutions of compound 1 (Fig. 3). We have measured the cyclic voltammogram of the K2As7 cluster also, for comparing the electrochemical behavior with compound 1 (Fig. S3†).17 The oxidation/reduction potentials of As73–/As72– are −0.15 V and −0.5 V vs. Ag+/Ag reference electrode (Fig. S3†). The cyclic voltammogram of compound 1 is distinctly different from the K2As7 cluster. Control experiments with only solvent/electrolyte (dashed line) did not show any redox active impurities in the solvent or the electrolyte.

We measured the optical band gap energy of compound 1 using diffuse reflectance spectroscopy, and the Kubelka–Munk model.18 This two-flux model, which considers only diffuse light, is generally used to determine the absorption coefficients from a surface that both scatters and absorbs incident radiation. For a crystalline solid with a nonzero band gap ($E_{bg}$), the frequency dependence ($\nu$) of the absorption coefficient ($\kappa$) can be approximated as:

$$\kappa(\nu) = \frac{B_\nu (h\nu - E_{bg})^n}{h\nu},$$

where $B_\nu$ is a constant derived from the square of the averaged dipolar momentum matrix element, and $n$ is equal to 0.5 and 2 for direct and indirect band gap transitions, respectively.19 Using the above equation, the band gap of a material can be obtained by extrapolating to the x-axis intercept with a linear fit to a plot of $(xh\nu)^{1/n}$ vs. $h\nu$. Fig. 4 shows the Tauc plot for compound 1. Optical measurements indicate that the band gap energy is approximately 1.67 ± 0.04 eV and compares favorably with the calculated band gap energy of 1.72 eV.

As compound 1 is an unusual dimer, the Raman spectra were recorded in the form of ground single crystals using a confocal Raman microscope to identify low energy vibrational modes. The Raman spectrum of compound 1 is shown in Fig. 5a and it shows two distinct peaks at around 164 and 250 cm$^{-1}$. To understand the origin of the peaks we have calculated the Raman spectra of compound 1 by quantum chemical methods. The
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Notes and references

§Synthesis: In a scintillation vial, 1 ml en solution of Hg(C6H5)2 (18 mg, 0.05 mmol) was added drop wise to a 2 ml en solution of K3As7 (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 filtered dark red suspension was layered with THF to allow for crystallization. After 2 d, a few dark red rod-like crystals of [K-Crypt]4[Hg2(As7)2], 1, formed on the wall of the test tube.

Crystal data: Mf = 3119.44, space group Pna2(1) (no. 33), a = 14.029 (3) Å, b = 21.253(5) Å, c = 43.606(10) Å, V = 12839(5) Å3, Z = 4, μcalc = 1.610 g cm−3, μ = 6.154 mm−1, 68 784 measured reflections, 23 541 unique reflections, R1 = 0.0642 and wR2 = 0.1168 for I > 2σ(I).


Fig. 4 Tauc plot showing the band gap energy determined from the optical absorption spectra (see text) of [K-crypt]4[Hg2(As7)2], 1.

Fig. 5 (a) Experimental Raman spectra of 1. (b) Simulated Raman spectra of the [Hg2(As7)2]4− anion.
