



# **[Sn<sub>9</sub>HgSn<sub>9</sub>]<sup>6-</sup>: An Intermetalloid Zintl Ion with Two Sn<sub>9</sub> Connected by Heteroatom**

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# **[Sn<sub>9</sub>HgSn<sub>9</sub>]<sup>6-</sup>: An Intermetalloid Zintl Ion with Two Sn<sub>9</sub> Connected by Heteroatom**

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Dedicated to Prof. Kniep on the Occasion of his 65<sup>th</sup> Birthday

**Keywords:** Zintl ion; Tin; Mercury; Cluster compound; Crystal structure

## **Abstract**

The title compound [K([2,2,2]crypt)]<sub>12</sub>[Sn<sub>9</sub>]<sub>2</sub>[Sn<sub>9</sub>HgSn<sub>9</sub>] has been obtained by reaction of elemental mercury with the binary phase K<sub>4</sub>Sn<sub>9</sub> in ethylenediamine after addition of [2,2,2]crypt and layering with toluene. The X-ray single crystal analysis shows that the compound consists of two isolated Sn<sub>9</sub> clusters and two Sn<sub>9</sub> clusters connected by a mercury atom.

## Introduction

Homoatomic-element polyhedra of the type  $E_n^{x-}$  ( $E$  = Group 14 element) are promising candidates for the formation of ligand-free intermetalloid clusters<sup>[1]</sup>. The introduction of a second metal to the polyhedral framework might occur via complexation to an organometallic metal fragment such as  $[\text{Ir}(\eta^4\text{-E}_9)(\text{cod})]^{3-}$  ( $E = \text{Sn, Pb}$ )<sup>[2]</sup>,  $[\text{Ge}_9\text{-Ni}(\text{CO})]^{3-}$ <sup>[3]</sup>,  $[\text{Cu}(\eta^4\text{-Ge}_9)(\text{P}^i\text{Pr})_3]^{3-}$ <sup>[4]</sup>,  $[\text{Zn}(\eta^4\text{-E}_9)(\text{R})]^{3-}$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $E = \text{Si-Pb}$ <sup>[5]</sup>;  $\text{R} = ^i\text{Pr, Mes}$ ,  $E = \text{Ge-Pb}$ <sup>[6]</sup>),  $[\text{Pd}(\eta^4\text{-Ge}_9)(\text{PPh}_3)]^{3-}$ <sup>[7]</sup>,  $[\text{Cd}(\eta^4\text{-E}_9)(\text{C}_6\text{H}_5)]^{3-}$  and  $[\text{Cd}(\eta^4\text{-Sn}_9)(\text{Sn}^n\text{Bu}_3)]^{3-}$ <sup>[8]</sup>. The first examples of ligand free heteroatomic clusters was reported in form of a linear polymeric chain  ${}^\infty[\text{HgGe}_9]^{2-}$  in which Hg atoms act as bridges between the  $\text{Ge}_9$  clusters<sup>[9]</sup>. Recently an oligomeric extract  $[\text{Hg}_3(\text{Ge}_9)_4]^{10-}$  of the polymeric chain has also been reported<sup>[10]</sup>. Up to now many attempts to prepare heteroatomic linked  $\text{Sn}_9$  clusters have been unsuccessful in solution chemistry. A comparable attempt using Te atoms to link  $\text{Sn}_9$  leads to the breakdown of the cluster and formation of the heteroatomic ions  $[\text{Te}_2\text{Sn}(\mu_2\text{-Te})_2\text{SnTe}_2]^{4-}$  and  $[\text{Sn}(\mu_2\text{-Te})_3\text{Sn}]^{2-}$ <sup>[11]</sup>. It is worth noting that the homoatomic oligomers of  $\text{Sn}_9$  are also unknown though their corresponding  $\text{Ge}_9$  have been reported successively in the last several years<sup>[12]</sup>.

Our reinvestigation of the reaction of elementary Hg with  $\text{Sn}_9$  clusters in analogy to the  $\text{Ge}_9$  clusters<sup>[9]</sup> by careful use of slow diffusion techniques resulted in the growth of black column crystals containing two isolated  $\text{Sn}_9$  cluster ions and one  $[\text{Sn}_9\text{HgSn}_9]^{6-}$  ion (Figure 1).

## Results and Discussion

Single X-ray diffraction measurement<sup>[13]</sup> reveals the formulae  $[\text{K}([2,2,2]\text{crypt})]_{12}[\text{Sn}_9]_2[\text{Sn}_9\text{HgSn}_9]$  (Figure 1), which consists of two isolated  $\text{Sn}_9$  clusters and two  $\text{Sn}_9$  clusters being connected by a mercury atom. The twelve  $[\text{K}([2,2,2]\text{crypt})]^+$  cations do not show any coordination to the  $\text{Sn}_9$  cluster anions.

For nine-atom clusters, the ratio  $h/e$  of prism heights  $h$  (**A**: Sn19-Sn21, Sn25-Sn26, Sn23-Sn24; **B**: Sn28-Sn30, Sn32-Sn33, Sn34-Sn35) to prism edge  $e$  of a  $D_{3h}$  symmetric tricapped trigonal prismatic structure, and the ratio of the two diagonals  $d$  (**A**: Sn19-Sn21, Sn20-Sn22, **B**: Sn28-Sn30, Sn29-Sn31) in the open rectangular face of the  $C_{4v}$  symmetric mono-capped square-

antiprism provides the best correlation of configuration with electron count<sup>[14, 15]</sup>. The two isolated nine atom clusters with virtual  $C_{2v}$  symmetry (Figure 2) adapt different shapes intermediate between the  $D_{3h}$  structure (*closo* type) and the mono-capped quadratic antiprismatic structure (*nido* type). In both anions one of the three heights of the underlying trigonal prism is elongated (**A**:  $d_{\text{Sn19-Sn21}} = 3.4546(9) \text{ \AA}$  versus  $3.2321(9) \text{ \AA}$ ,  $3.2162(9) \text{ \AA}$ ; **B**:  $d_{\text{Sn28-Sn30}} = 3.3426(8) \text{ \AA}$  versus  $3.2954(9) \text{ \AA}$ ,  $3.2607(9) \text{ \AA}$ ). Considering the longest prism height as non-bonding, the ratios of the diagonals of the distorted square are 1.37 and 1.44 for the clusters **A** and **B**, respectively, indicating a strong distortion from  $C_{4v}$  symmetry with expected values of 1.00. With average values of 3.300 and 3.301 for  $h$  and 3.074 and 3.066 for  $e$ , the  $h/e$  ratio of the clusters **A** and **B** is for both 1.07. Thus, the ratios are quite similar with those of  $\text{Sn}_9^{3-}$  ions in  $[\text{K}([2.2.2]\text{crypt})]_3\text{Sn}_9 \cdot 1.5\text{en}^{[14]}$  and of  $[\text{K}([2.2.2]\text{crypt})]_3\text{Sn}_9 \cdot 0.5\text{en}^{[16]}$  having values of 1.08 and 1.07, respectively.

In the  $[\text{Sn}_9\text{HgSn}_9]^{6-}$  anion, two  $\text{Sn}_9$  clusters **C** and **D** are connected by the Hg atom (Figure 3). The anion has nearly a center of inversion at the Hg atom position and the  $\text{Sn}_9$  clusters adapt to distorted tricapped trigonal prisms with approximately  $C_{2v}$  symmetry. The Sn-Sn bond lengths range from  $2.9134(9) \text{ \AA}$  to  $3.2889(9) \text{ \AA}$  and are in accordance with those known in other  $\text{Sn}_9^{[17]}$  and  $\text{Sn}_6^{[18]}$  clusters. In both  $\text{Sn}_9$  clusters one of the three heights of the underlying trigonal prism is shorter ( $d_{\text{Sn5-Sn6}} = 3.2652(9) \text{ \AA}$  versus  $3.4184(9) \text{ \AA}$ ,  $3.5636(9) \text{ \AA}$  for **C**;  $d_{\text{Sn16-Sn17}} = 3.2889(9) \text{ \AA}$  versus  $3.5496(9) \text{ \AA}$ ,  $3.4413(9) \text{ \AA}$ ) in **D**). With average values of 3.416 and 3.427 for  $h$  and 3.051 and 3.045 for  $e$ , the  $h/e$  ratio of the clusters is 1.12 and 1.13. The elongation of the three prismatic edges Sn1-Sn3, Sn5-Sn6 and Sn7-Sn8 and Sn10-Sn12, Sn14-Sn15 and Sn16-Sn17 in these  $\text{Sn}_9$  clusters account also for the additional contacts to Hg atoms. The  $\text{Sn}_9$  clusters coordinate via two triangular faces to the Hg atom, each with two shorter ( $d_{\text{Sn1-Hg}} = 3.0438(8) \text{ \AA}$ ,  $d_{\text{Sn8-Hg}} = 3.0834(7) \text{ \AA}$  in **C**;  $d_{\text{Sn10-Hg}} = 3.0114(7) \text{ \AA}$ ,  $d_{\text{Sn14-Hg}} = 3.1530(8) \text{ \AA}$  in **D**) and one longer contact ( $d_{\text{Hg-Sn5}} = 3.4559(7) \text{ \AA}$  in **C**;  $d_{\text{Hg-Sn17}} = 3.4132(7) \text{ \AA}$  in **D**). These bond lengths are somewhat longer than the sum of their respective covalent radii ( $2.84 \text{ \AA}$ )<sup>[19]</sup> reflecting the high coordination number of the Hg atom. Due to the interaction with the Hg atom, the triangular face made of atoms Sn1, Sn5, Sn8 is enlarged ( $d_{\text{Sn1-Sn8}} = 3.0429(8)$ ,  $d_{\text{Sn1-Sn5}} = 3.1116(8)$ ,  $d_{\text{Sn5-Sn8}} = 3.0794(8)$ ) with respect to the opposite triangular face made of Sn3, Sn6, Sn7 ( $d_{\text{Sn3-Sn7}} = 2.9608(8)$ ,  $d_{\text{Sn3-Sn6}} = 3.0750(9)$ ,  $d_{\text{Sn6-Sn7}} = 3.0350(8)$ ). The Sn atoms with the weakest interaction with Hg (Hg-Sn5, Hg-Sn17) form the shortest prismatic edge ( $d_{\text{Sn5-Sn6}} = 3.2652(9) \text{ \AA}$ ,  $d_{\text{Sn16-Sn17}} = 3.2889(9) \text{ \AA}$ ). The Hg atom is coordinated by the four nearest Sn atoms Sn1, Sn8, Sn10 and Sn14 in a rectangular-

planar fashion with the mercury atom lying in the plane of those tin atoms. The bond angles of Sn1-Hg-Sn10 and Sn8-Hg-Sn14 are 176.4° and 176.6° respectively and hence close to 180°. A rectangular or square-planar coordination is rather uncommon but has been observed for Hg(II) complexes.<sup>[20]</sup> In [Sn<sub>9</sub>HgSn<sub>9</sub>]<sup>6-</sup> to further and longer Hg-Sn contacts occur resulting in a strongly distorted trigonal anti-prismatic coordination polyhedra. with Sn5-Hg-Sn17 bond angle of 174.9°<sup>[21]</sup>.

Since the product contains [K([2,2,2]crypt)]<sub>6</sub>[Sn<sub>9</sub>]<sub>2</sub> · 1.5 en · 0.5 tol<sup>[22]</sup> as paramagnetic impurity the spin state of the title compound could not be determined unambiguously and the charge allocation is not obvious. Due to their similarity to other known [Sn<sub>9</sub>]<sup>3-</sup> ions, we assume the two isolated clusters carry a charge of -3 as well. That postulates a [Sn<sub>9</sub>HgSn<sub>9</sub>]<sup>6-</sup> anion. In analogy to <sup>1</sup>[HgGe<sub>9</sub>]<sup>2-</sup> formal oxidation states for Hg of +2 and 0 according to ([Sn<sub>9</sub>]<sup>4-</sup>)Hg<sup>2+</sup>([Sn<sub>9</sub>]<sup>4-</sup>) and ([Sn<sub>9</sub>]<sup>3-</sup>)-Hg-([Sn<sub>9</sub>]<sup>3-</sup>) can be assigned.

In the polymers <sup>1</sup>[HgGe<sub>9</sub>]<sup>2-</sup><sup>[9]</sup> the Hg atoms is linearly coordinated to one Ge atom of each of the two neighboring Ge<sub>9</sub> clusters. In the oligomer [Hg<sub>3</sub>(Ge<sub>9</sub>)<sub>4</sub>]<sup>10-</sup><sup>[10]</sup> the same holds for the central Hg atom, whereas the coordination to the terminal Ge<sub>9</sub> clusters is of η<sup>2</sup> fashion resulting in three nearest Hg-Ge contacts.

## Conclusion

Our investigations showed the preparation of heteroatomic linked Sn<sub>9</sub> clusters in solution chemistry is possible, analogous to those of germanium. The rectangular planar coordination of Hg by four Sn atoms hints for a Hg(II) compound and thus differs the coordination of the Hg atom from the related compounds containing Ge<sub>9</sub>HgGe<sub>9</sub> building blocks.

## Experimental Section:

The synthesis of compound **1** was carried out under argon atmosphere using a glove-box or Schlenk line. Toluene (Merck) and ethylenediamine (Merck) were dried over CaH<sub>2</sub> (Fluka), freshly distilled and degassed. The binary phase of the formal composition “K<sub>4</sub>Sn<sub>9</sub>” was prepared by high-temperature reaction (650 °C) from the elements K and Sn in the ratio of 4:9.

K<sub>4</sub>Sn<sub>9</sub> (200 mg, 0.164 mmol) and [2,2,2]crypt (246 mg, 0.65 mmol) were dissolved in ethylenediamine (ca. 2 ml) in a 25 ml Schlenk tube and stirred for 5 min to yield a dark red solution. Then Hg (200mg, 1mmol) was added dropwise at room temperature. The resulting mixture was stirred for another 2 hours at room temperature to yield a reddish-brown solution. Afterwards the reaction was treated for 20 min. in an ultrasonic bath, and then filtered. The filtrate was layered with toluene (2 mL). After 48 hours, dark column crystals contains [K([2,2,2]crypt)]<sub>12</sub>[Sn<sub>9</sub>]<sub>2</sub>[Sn<sub>9</sub>HgSn<sub>9</sub>] precipitated with the yield of 50 mg, (ca. 35% with respect to K<sub>4</sub>Sn<sub>9</sub>). The EDX analysis of crystal shows the existence of elements K, Hg and Sn with approximately the expected ratio of these elements of 12:1:36. [K([2,2,2]crypt)]<sub>6</sub>[Sn<sub>9</sub>]<sub>2</sub> · 1.5 en · 0.5 tol<sup>[22]</sup> was obtained as byproduct as shown by lattice parameter determination of single crystals.

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[13] Crystal structure determination: Crystals were mounted in glass capillaries. Structure solution (SHELX-97 and refinement SHELXL-97) was carried out with direct methods and full-matrix least-square methods based on  $F^2$  for non-hydrogen atoms with anisotropic displacement parameters, except for the atoms of five crypt molecules. Due to disorder their non-hydrogen atoms were splitted using JANA2006 (Petricek, V., Dusek, M. & Palatinus, L.). The corresponding atoms were labeled with ' and were refined with equal isotropic displacement parameters. Due to disorder of the solvent molecules, their contribution to the structure factors were modeled using the SQUEEZE option in PLATON. All hydrogen atoms were calculated using a riding model. Crystal dimensions: 0.4 x 0.4 x 0.2 mm. Lattice constants at 120 K:  $a=27.8452(1)$  Å,  $b=28.3340(1)$  Å,  $c=28.9569(2)$  Å  $\alpha=68.4618(2)^\circ$ ,  $\beta=69.7966(2)^\circ$ ,  $\gamma=61.3741(3)^\circ$ ,  $V=17870.26(7)$  Å<sup>3</sup>; space group P-1 (No. 2);  $Z=2$ ,  $\rho_{\text{calcd}}=1.833$  g/cm<sup>3</sup>,  $\mu=3.097$  mm<sup>-1</sup>; Data collection: Nonius Kappa CCD device at the window of a rotating anode X-ray generator;  $\text{Mo}_{\text{K}\alpha}$  radiation,  $2\theta_{\text{max}}=46.49$ ; 190950 total reflections, 50908 were independent reflections; completeness to  $\theta$  99.2 %; multi-scan absorption correction. ( $R_{\text{int}}=0.086$ ),  $R_1=0.053$ , and  $wR_2=0.090$  with  $F^2>2$  ( $\theta(F^2)$ ),  $R_1=0.095$  and  $wR=0.102$  for all data, respectively. CCDC-767025 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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[21] Sn-Sn distances [ $\text{\AA}$ ] in  $[\text{Sn}_9\text{HgSn}_9]^{6-}$  anion: Sn10-Sn11 2.9308(9), Sn10-Sn13 2.937(1), Sn10-Sn14 3.0325(8), Sn10-Sn17 3.0675(9), Sn11-Sn14 2.9295(9), Sn10-Sn12 3.5496(9), Sn11-Sn15 2.9717(8), Sn11-Sn12 2.994(1), Sn12-Sn13 2.960(1), Sn12-Sn15 2.9713(8), Sn12-Sn16 3.0455(9), Sn13-Sn17 2.9412(9), Sn13-Sn16 2.9534(9), Sn14-Sn18 2.9384(9), Sn14-Sn17 3.1176(9), Sn14-Sn15 3.4413(9), Sn15-Sn18 2.9565(9), Sn15-Sn16 3.0324(9), Sn16-Sn18 2.9510(9), Sn16-Sn17 3.2889(9), Sn17-Sn18 2.9545(8), Sn1-Sn2 2.9236(9), Sn1-Sn4 2.9414(9), Sn1-Sn8 3.0429(8), Sn1-Sn5 3.1116(8), Sn1-Sn3 3.4184(9), Sn2-Sn5 2.9414(8), Sn2-Sn6 2.9569(9), Sn2-Sn3 2.9646(9), Sn3-Sn7 2.9608(8), Sn3-Sn4 2.9895(9), Sn3-Sn6 3.0750(9), Sn4-Sn8 2.9134(9), Sn4-Sn7 2.9649(8), Sn5-Sn9 2.9568(8), Sn5-Sn8 3.0794(8), Sn5-Sn6 3.2652(9), Sn6-Sn9 2.9633(8), Sn6-Sn7 3.0350(8), Sn7-Sn9 2.9747(9), Sn7-Sn8 3.5636(9), Sn8-Sn9 2.9389(8); Sn-Hg-Sn- angles [ $^\circ$ ]: Sn10-Hg-Sn14 58.88(2), Sn10-Hg-Sn17 56.63(2), Sn14-Hg-Sn17 56.52(2), Sn1-Hg-Sn8 59.55(2), Sn1-Hg-Sn5 56.78(2), Sn5-Hg-Sn8 55.84(2), Sn1-Hg-Sn10 176.39(2), Sn8-Hg-Sn14 176.55(2), Sn5-Hg-Sn17 174.91(2)

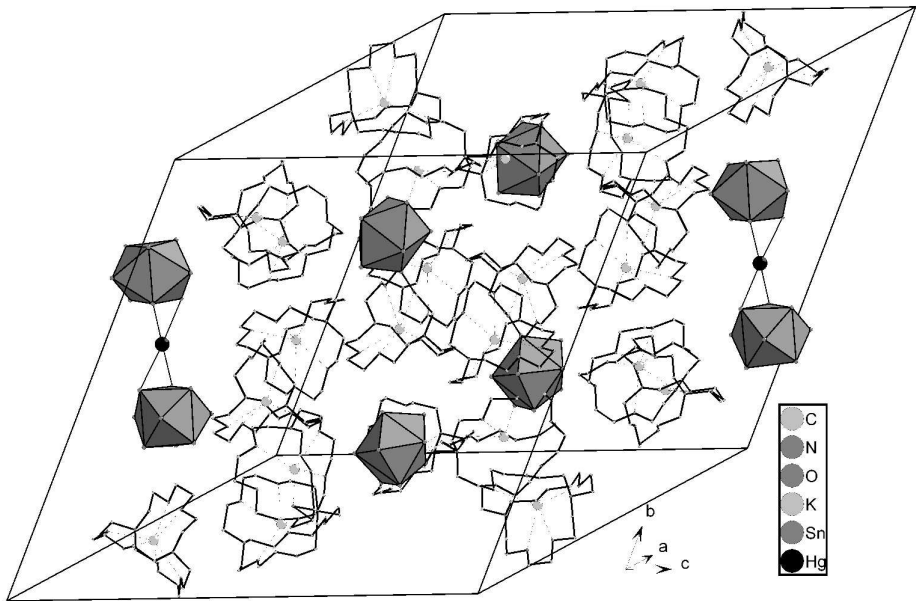
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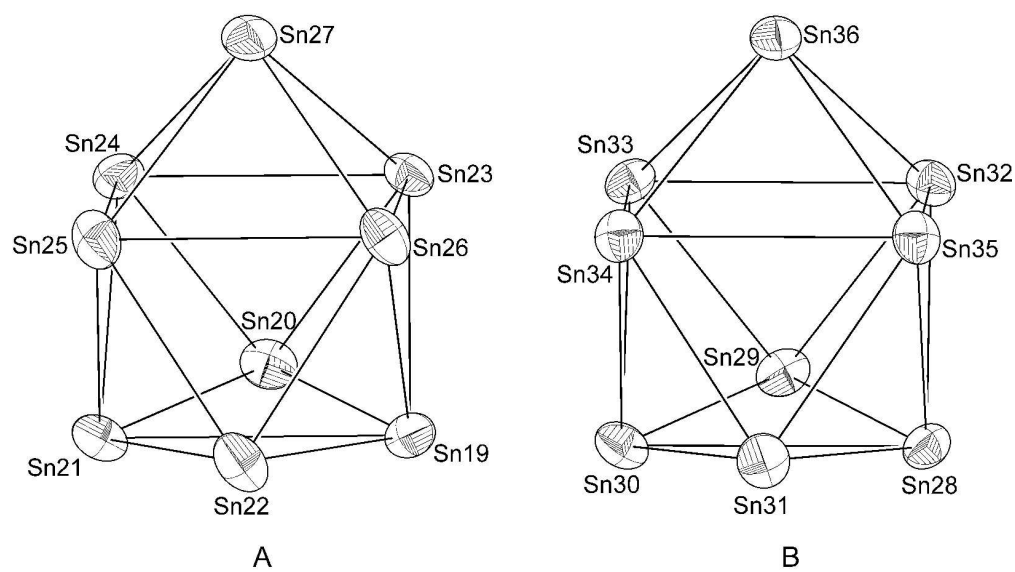
## Figure Captions

**Figure 1.** The isolated  $[\text{Sn}_9]^{3-}$  ion and isolated  $[\text{Sn}_9\text{HgSn}_9]^{6-}$  ion are represented in unit cell as polyhedra. The isolated  $[\text{Sn}_9]^{3-}$  ions and  $[\text{Sn}_9\text{HgSn}_9]^{6-}$  ion are emphasized in Figure 2 and Figure 3, respectively.

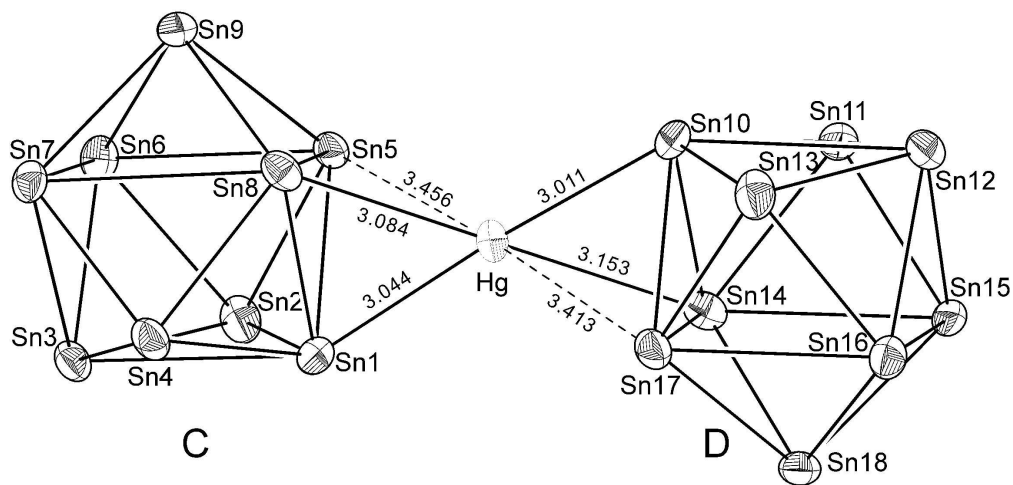
**Figure 2.** View of the isolated  $\text{Sn}_9^{3-}$  anions. (Thermal ellipsoids are shown at 50 % probability level.)

**Figure 3.** Section of the molecular structure of  $[\text{Sn}_9\text{HgSn}_9]^{6-}$  ion. (atomic displacement vectors are set at 50 % probability). Some important interatomic distances ( $\text{\AA}$ ) and angles [ $^\circ$ ]:  $d_{\text{Hg-Sn1}} = 3.0438(8)$ ,  $d_{\text{Hg-Sn8}} = 3.0834(7)$ ,  $d_{\text{Hg-Sn10}} = 3.0114(7)$ ,  $d_{\text{Hg-Sn14}} = 3.1530(8)$ ,  $\text{Sn1-Hg-Sn10}$   $176.39(2)^\circ$ ,  $\text{Sn8-Hg-Sn14}$   $176.55(2)^\circ$ . For further distances and angles, see text and reference <sup>[21]</sup>.





275x155mm (600 x 600 DPI)



194x98mm (600 x 600 DPI)