

Two Novel Lead Zintl Clusters within the Same Compound

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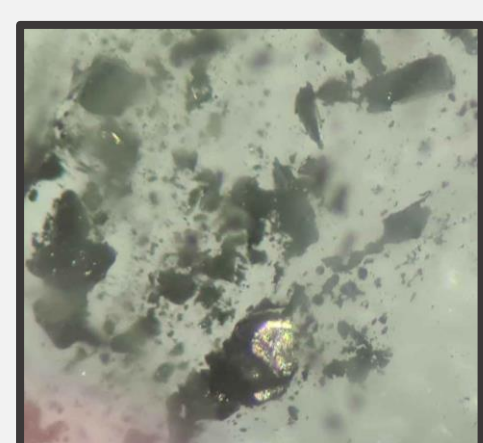
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Polyanionic clusters of group 14 elements are often categorized as Zintl anions.^[1] They are prepared either by solid state synthesis of the alkali metal phases and subsequent dissolution in polar solvents, or by the direct reduction of Sn or Pb in liquid ammonia. These isolated clusters can then be functionalized with heteroatoms, most commonly in the form of transition metal complexes. The heavier homologues can exhibit cluster growth leading to the formation of endohedral clusters containing transition metal centers.^[2] On this poster we present the crystal structure of $[\text{Rb}([\text{2.2.2}]\text{crypt})]_4\text{Rb}_{3.67}[\text{Au}_2\text{Pb}_{10}]_{1.67}[\text{Au}@\text{Pb}_{11}]_{0.33} \cdot 22 \text{NH}_3$ containing the two novel plumbide anions $[\text{Au}_2\text{Pb}_{10}]^{4-}$ and $[\text{Au}@\text{Pb}_{11}]^{3-}$.

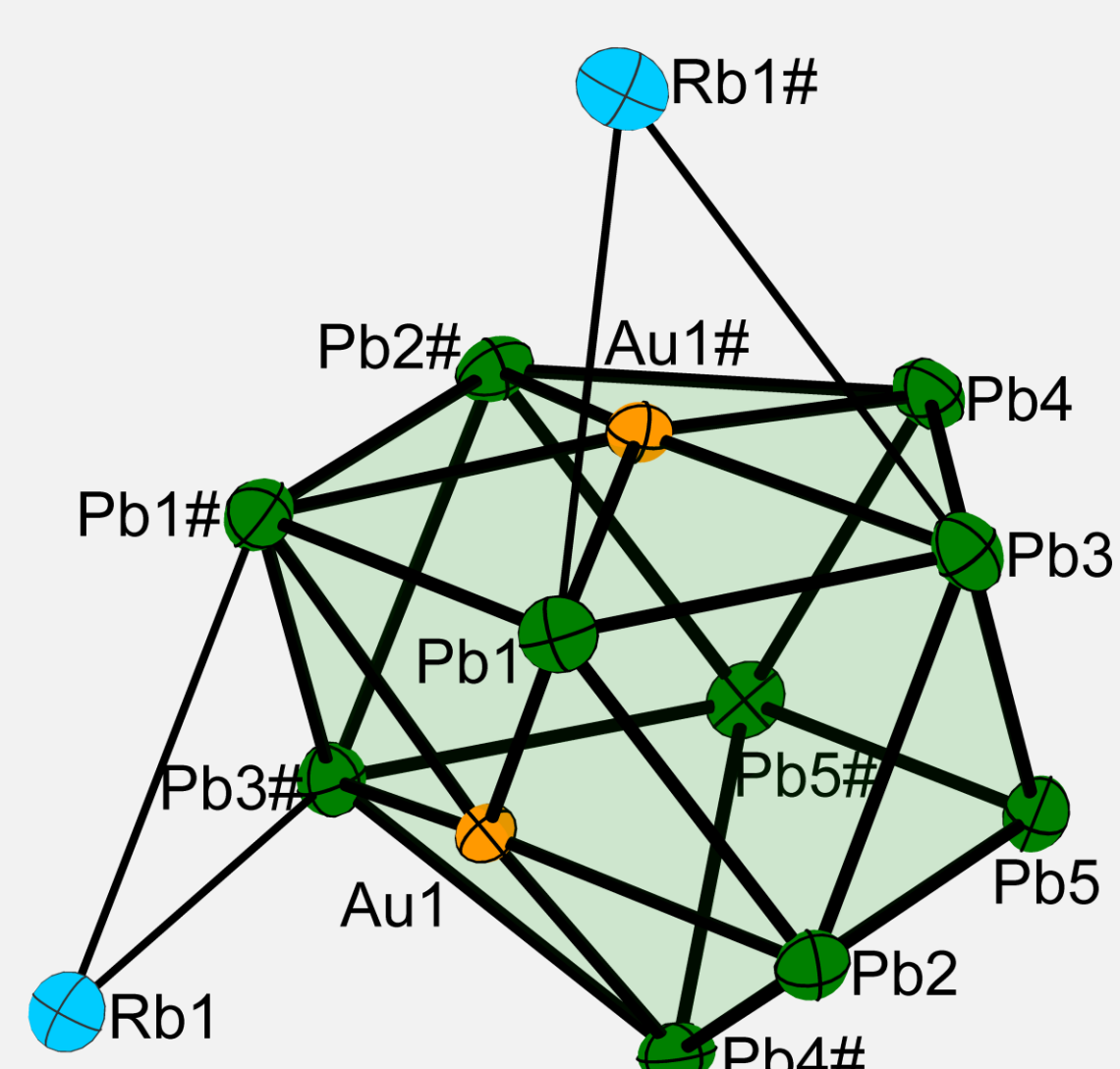
Synthesis



The reactants are dissolved in liquid ammonia and stored at -40°C . After 18 months black, block like crystals are obtained.

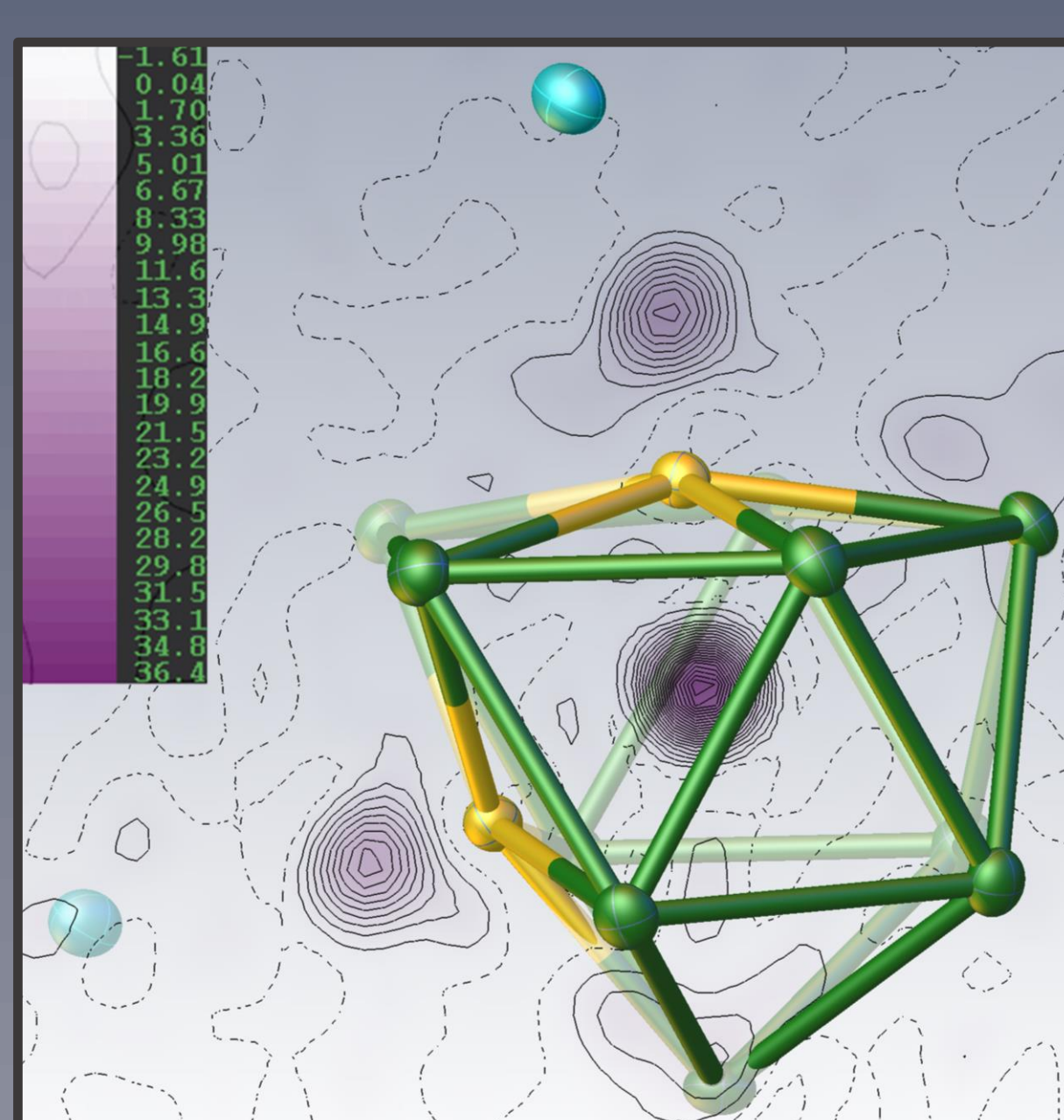


The Main Anion $[\text{Au}_2\text{Pb}_{10}]^{4-}$



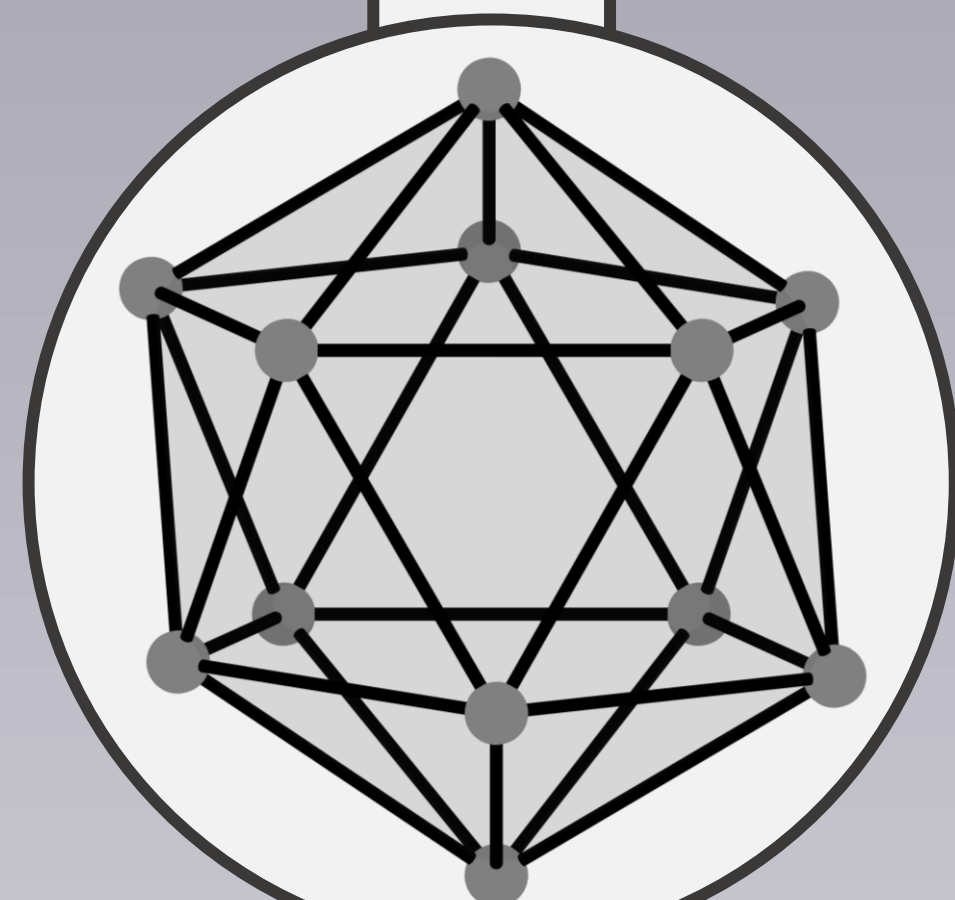
	$d_{\text{exp}} [\text{\AA}]$	$d_{\text{calc}} [\text{\AA}]$
$d(\text{Pb}-\text{Pb})$	3.1668(10) – 3.3356(9)	3.1014 – 3.2613
$d(\text{Pb}-\text{Au})$	2.7911(9) – 2.8335(8)	2.7331 – 2.7509
$d(\text{Au}-\text{Au})$	3.1097(10)	2.8386

- Rearrangement of $[\text{Pb}_4]^{4-}$ in the presence of Au(I) to an icosahedron-like cluster with two vertices replaced by Au atoms, which are shifted towards the cluster center
- The anionic unit is generated from six atoms via a two-fold axis of the space group $P2/n$
- Au–Au distance indicative of Au(I) aurophilic interaction^[3]
- Free refinement of the site occupancy factor (SOF) reveals that Rb1 (SOF = 0.879(7)) and Au1 (SOF = 0.843(3)) are significantly underoccupied



High residual electron density in the cluster center and in the vicinity of Au1

Disorder due to the ball-like, near icosahedral geometry of all components

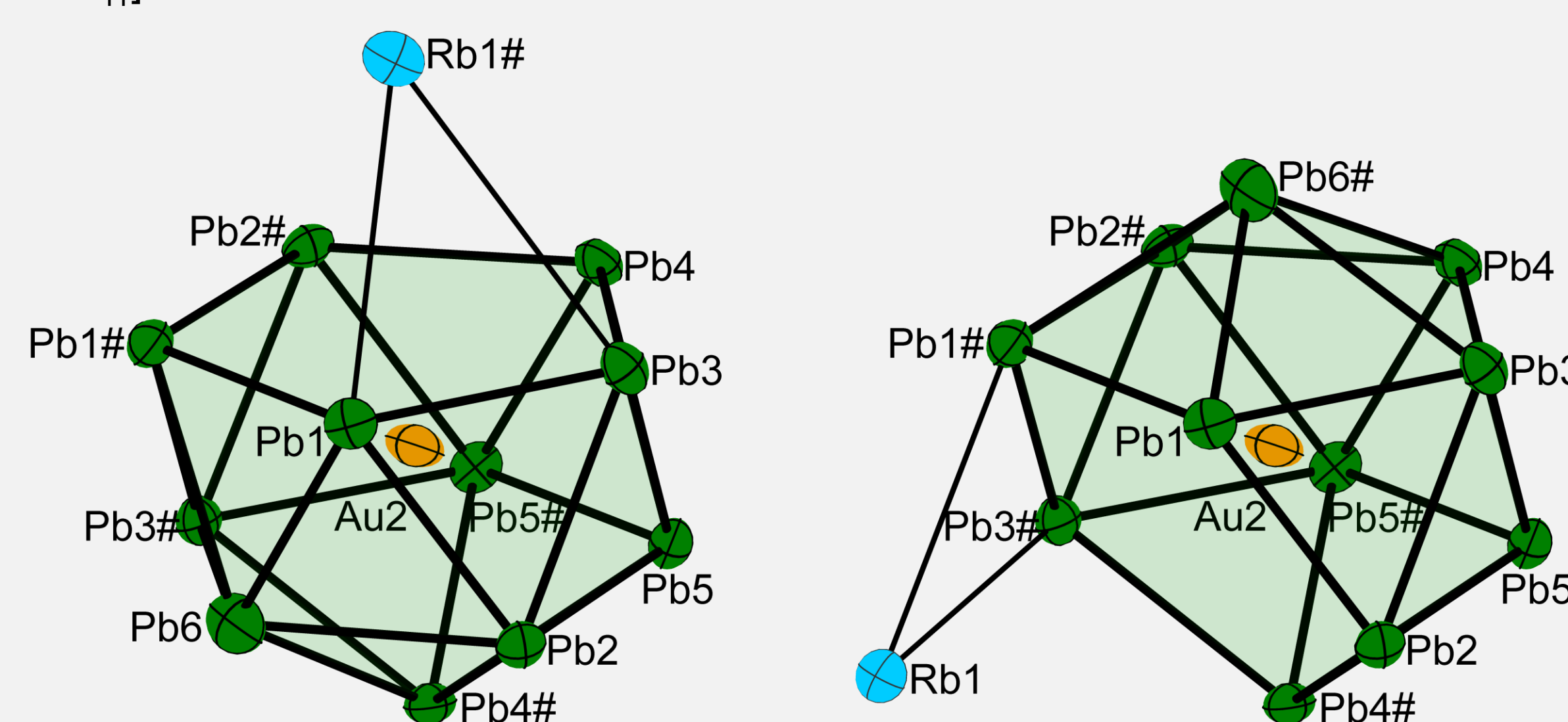


The Side Anion $[\text{Au}@\text{Pb}_{11}]^{3-}$

- The coordination environment of the residual electron density suggests a gold atom (Au2) in the cluster center and lead atoms (Pb6/Pb6#) at the cluster vertices
- Resulting distances Au1–Au2 and Pb6–Rb1 are too short for the respective positions to be occupied by both atoms at the same time

	$d_{\text{exp}} [\text{\AA}]$		Au1	Au2	Rb1	Pb6
$d(\text{Au2}-\text{Pb})$	2.987(9) – 3.142(5)					
$d(\text{Pb6}-\text{Pb})$	3.104(11) – 3.296(8)	SOF	0.843(3)	0.197(5)	0.879(7)	0.119(5)
$d(\text{Au1}-\text{Au2})$	1.844(3)					
$d(\text{Pb6}-\text{Rb1})$	2.422(9)					

- Free refinement of the SOF of Au2 supports inverse correlation with Au1
- Free refinement of the SOF of Pb6 supports inverse correlation with Rb1
- Occupancy variables of Au2 and Pb6 are close to a 2:1 ratio suggesting the presence of a $[\text{Au}@\text{Pb}_{11}]^{3-}$ cluster in two different orientations with either Pb6 or Pb6# as the eleventh vertex, replacing the alkali metal position Rb1 or Rb1# respectively
- Cluster geometry and presumed charge of (–III) analogous to the already known $[\text{Ag}@\text{Pb}_{11}]^{3-}$ ^[4]



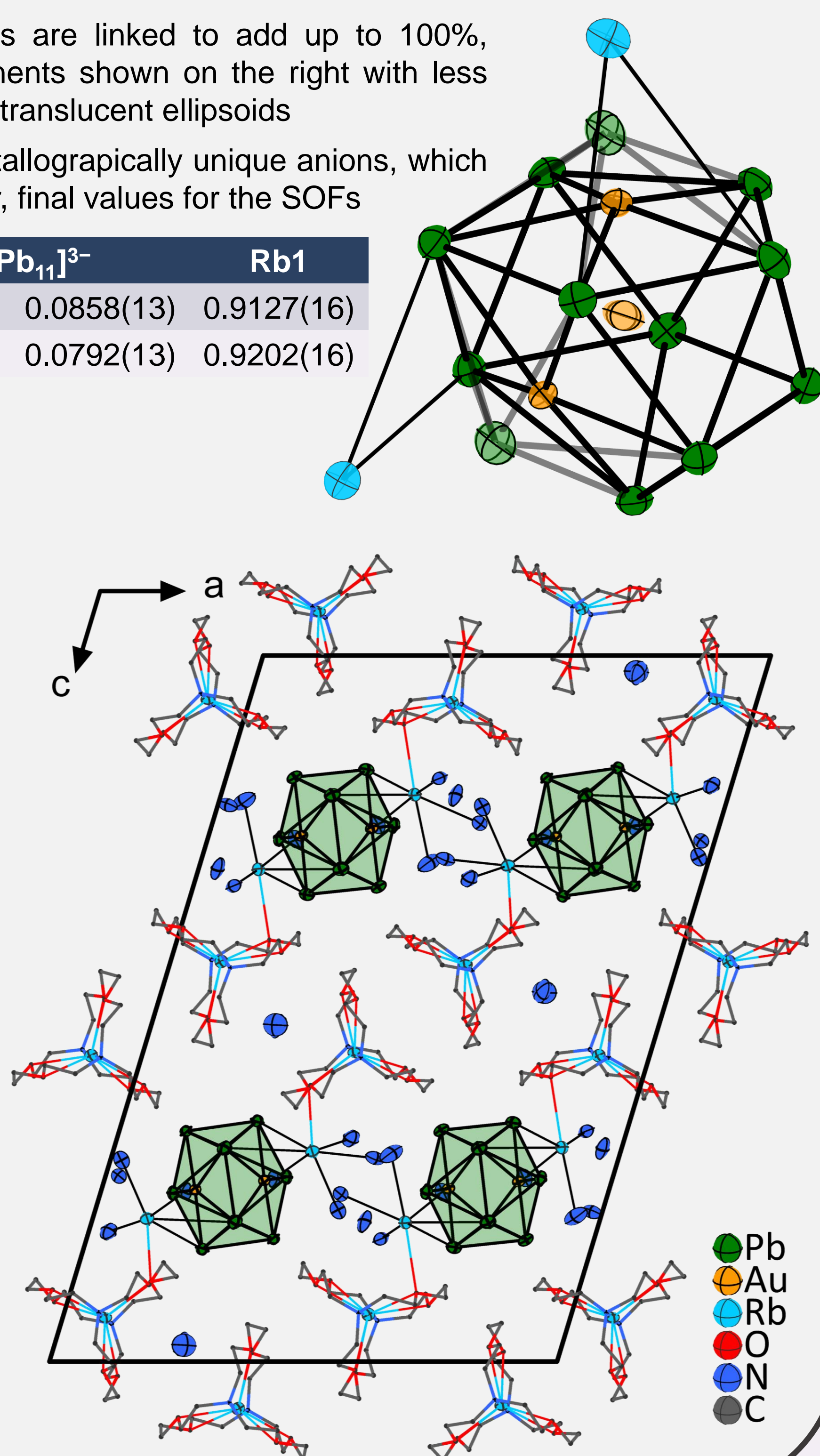
	$d_{\text{exp}} [\text{\AA}]$	$d_{\text{calc}} [\text{\AA}]$
$d(\text{Pb}-\text{Pb})$	3.104(11) – 3.3356(9)	2.9528 – 3.2365
$d(\text{Pb}-\text{Au})$	2.987(9) – 3.142(5)	2.7841 – 3.0661

$[\text{Rb}([\text{2.2.2}]\text{crypt})]_4\text{Rb}_{3.67}[\text{Au}_2\text{Pb}_{10}]_{1.67}[\text{Au}@\text{Pb}_{11}]_{0.33} \cdot 22 \text{NH}_3$

- The SOFs of the respective positions are linked to add up to 100%, yielding the superposition of all components shown on the right with less occupied positions represented as more translucent ellipsoids
- The asymmetric unit contains two crystallographically unique anions, which both show the same disorder with similar, final values for the SOFs

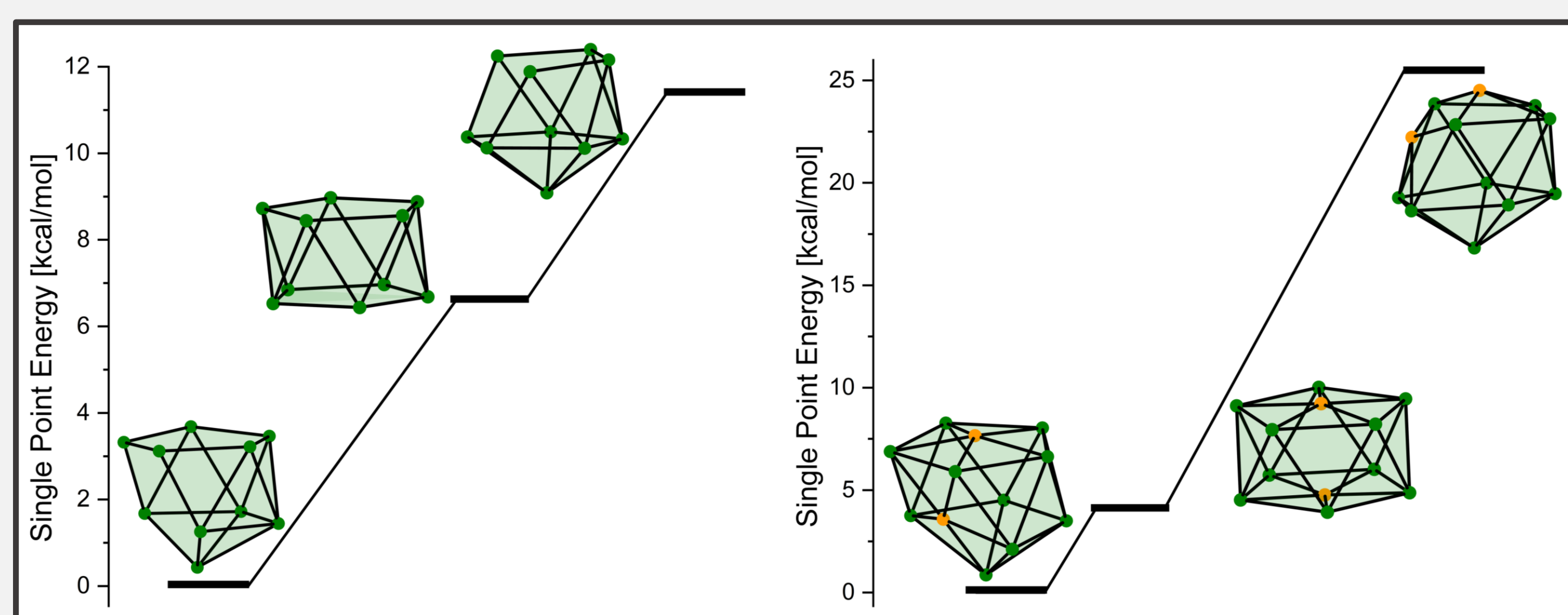
Final SOFs	$[\text{Au}_2\text{Pb}_{10}]^{4-}$	$[\text{Au}@\text{Pb}_{11}]^{3-}$	Rb1
Disorder 1	0.828(3)	0.0858(13)	0.9127(16)
Disorder 2	0.842(3)	0.0792(13)	0.9202(16)

Formula weight [g/mol]	7458.76
Crystal system	monoclinic
Space group	$P2/n$
a [Å]	22.5552(4)
b [Å]	11.4678(2)
c [Å]	32.7600(7)
β [°]	106.852(2)
Volume [Å ³]	8109.8(3)
Z, ρ [g/cm ³]	2, 3.054
μ [mm ⁻¹]	26.655
F(000)	6545.0
2 θ range	4.392 – 56.564
Crystal size [mm ³]	0.09x0.06x0.05
Temperature [K]	100.15(12)
Radiation, λ [Å]	Mo-K α , 0.71073
Index ranges	$30 \geq h \geq -30$, $15 \geq k \geq -15$, $43 \geq l \geq -43$
Ref. all/independent	69450/19942
Data/Restr./ Par.	19942/2/747
R_1, wR_2 ($F^2 \geq 2\sigma(F^2)$)	6.08 %, 17.08 %
R_1, wR_2 (all data)	8.89 %, 18.45 %
I/σ	15.8
R_{int}	7.96 %
Compl.	98.6 %
Goof	1.039
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ [e-Å ⁻³]	6.38/–4.25



Understanding the Formation of $[\text{Au}_2\text{Pb}_{10}]^{4-}$

- Similarly to other known coinage metal containing lead clusters, the Au cations can be considered as contributing a charge of (+I) to the net charge of the anion^[5]
- The remaining $[\text{Pb}_{10}]^{6-}$ anion is the result of the widely observed oxidation of highly reduced Zintl anions in liquid ammonia and should therefore not be accessible from $[\text{Pb}_3]^{4-}$ ^[6]
- The cluster takes the form of an icosahedron with two missing vertices, in accordance with the Wade-Mingos rules as an *arachno* cluster due to $n + 3$ skeletal bonding electron pairs^[7]
- However, for classical boron clusters the absence of two adjacent cluster vertices would be expected, which is not the case in the present anion
- Calculation of the single point energy for the different possible $[\text{Pb}_{10}]^{6-}$ isomers in their optimized geometry reveals that in comparison to the presented cluster the absence of two opposite or two adjacent vertices is energetically disfavored by 6.65 kcal/mol and 11.40 kcal/mol, respectively
- An analogous trend can be observed for the twice capped $[\text{Au}_2\text{Pb}_{10}]^{4-}$ anions. Capping on opposite or adjacent positions is energetically disfavored by 4.12 kcal/mol and 25.55 kcal/mol, respectively
- Therefore, the present anion represents the energetically most favorable isomer in contrast to the isoelectronic, bicapped pentagonal antiprism $[\text{Bi}_{10}\text{Au}_2]^{6+}$ in $[\text{Bi}_{10}\text{Au}_2](\text{SbBi}_3\text{Br}_9)_2$ ^[8]



Single point energies of different constitutional isomers of $[\text{Pb}_{10}]^{6-}$ (left) and $[\text{Au}_2\text{Pb}_{10}]^{4-}$ (right) after geometry optimization

All DFT calculations were carried out using M062X/jorge-TZP-DKH levels of theory as well as implementing a CPCM model with ammonia as the solvent.

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