

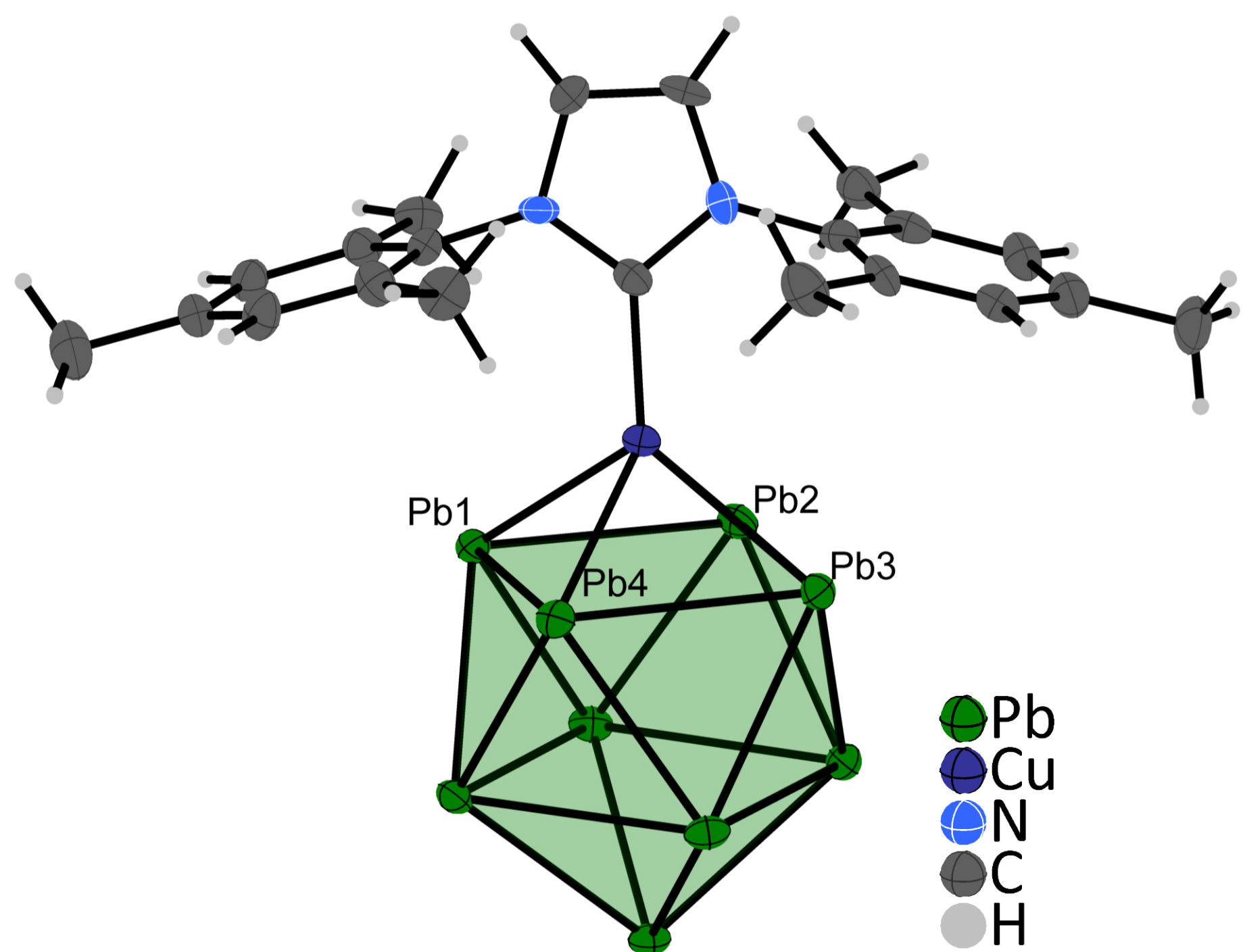
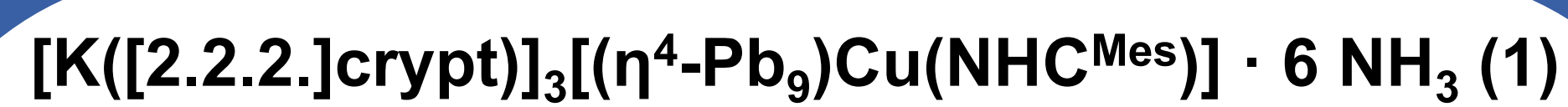
Novel Functionalized Lead Zintl Clusters from Liquid Ammonia

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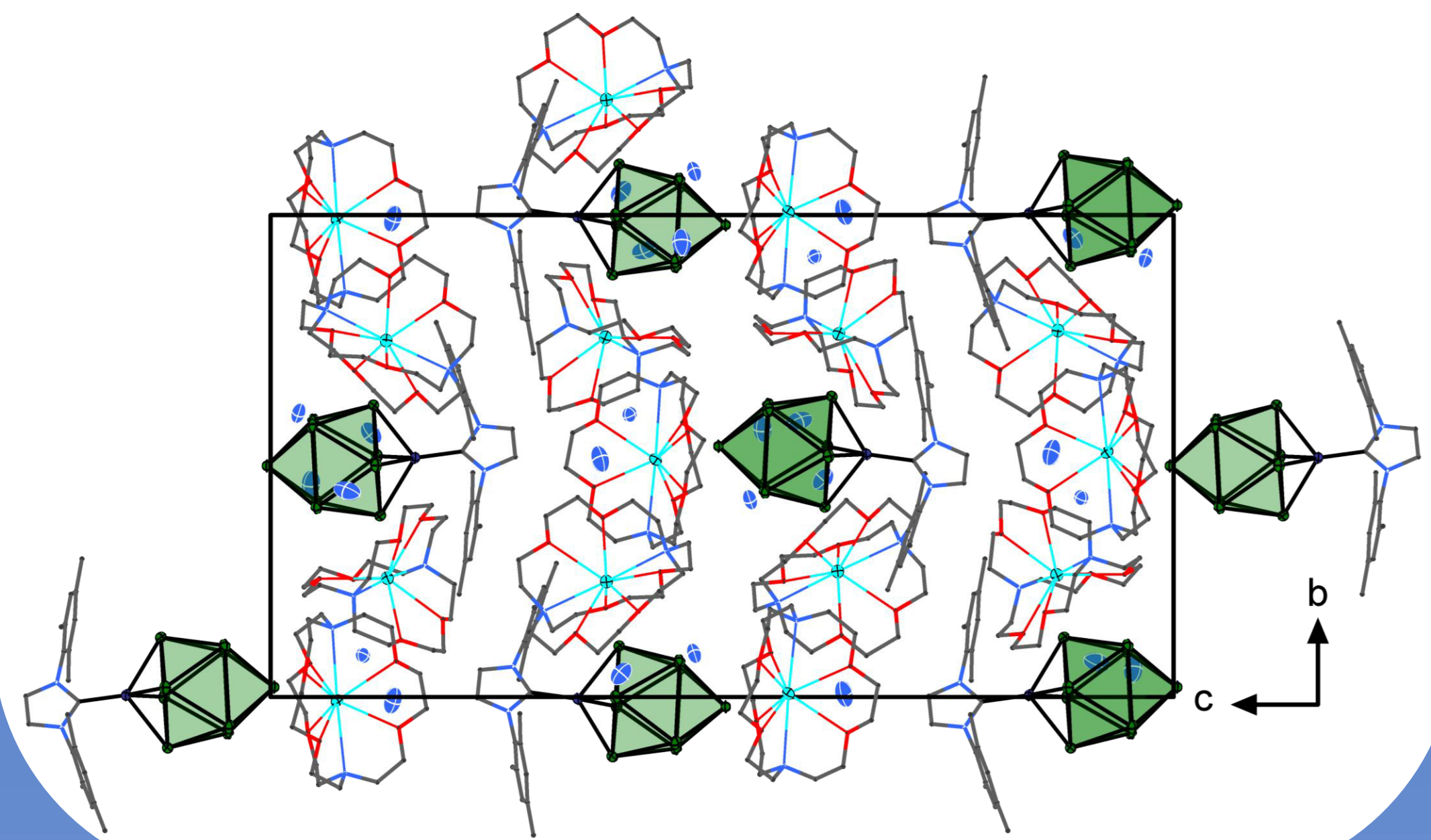
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Polyanionic clusters of group 14 elements are often categorized as *Zintl* anions.^[1] They are prepared either by solid state synthesis of the alkali metal phases and subsequent dissolution in polar solvents, or by the direct reduction of Sn or Pb in liquid ammonia. These isolated clusters can then be functionalized with heteroatoms. In the case of the tetrel clusters Tt_9^{4-} , which often take the shape of a monocapped square antiprism, the capping of the square face is the predominantly observed motif. Recent results were achieved using coinage metal NHC complexes for Si_9^{4-} - Sn_9^{4-} .^[2] In addition, plumbides can exhibit cluster growth leading to the formation of endohedral clusters containing transition metal centers.^[3]



	d_{exp} [Å]	d_{calc} [Å]
d(Pb—Pb)	3.0584(4) – 3.3653(5)	3.055 – 3.330
d(Pb—Cu)	2.7327(9) – 2.7786(10)	2.631 – 2.656
d(Cu—C)	1.946(7)	1.933

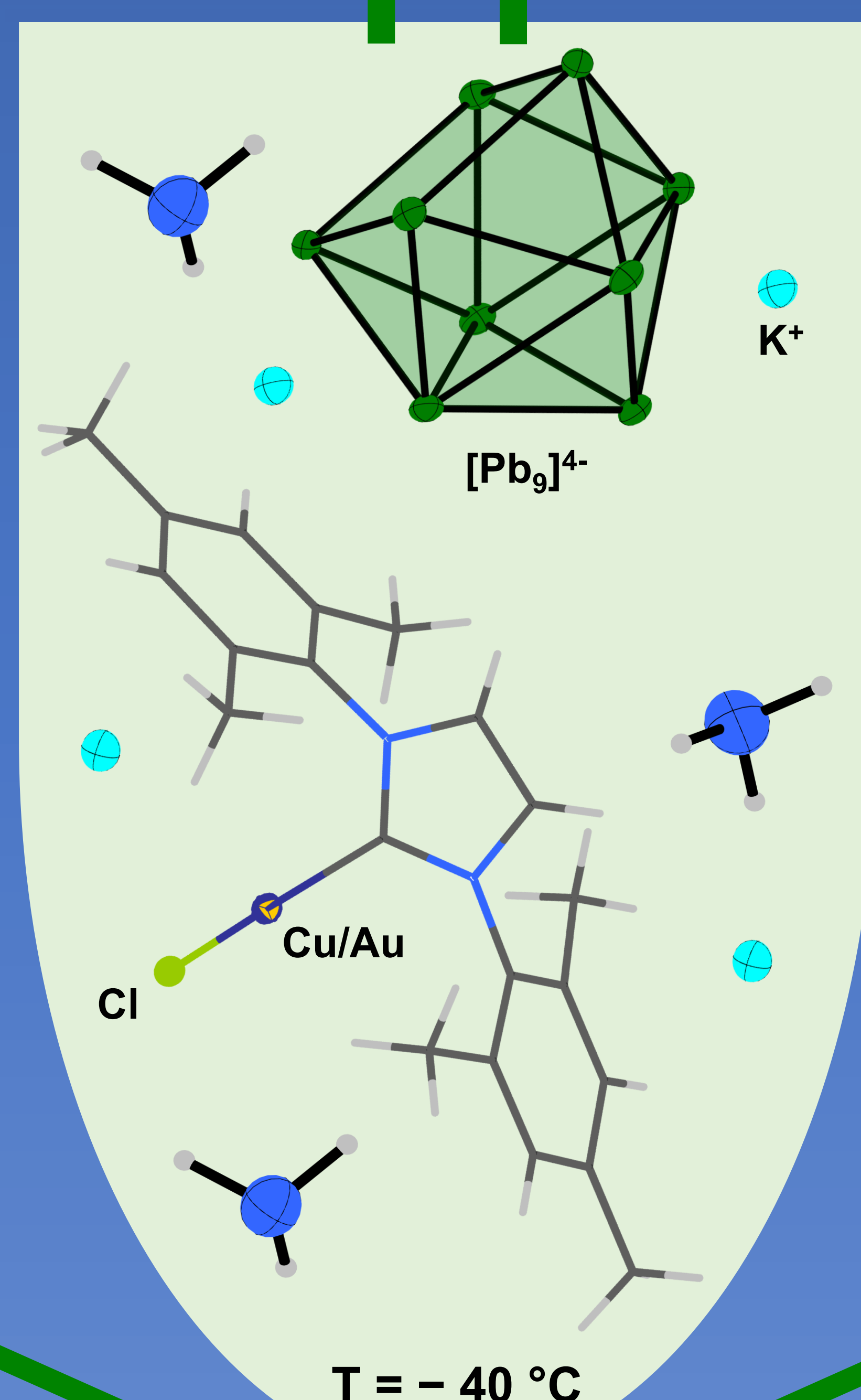
- Capping of the square face of $[Pb_9]^{4-}$ by the $[Cu(NHC^{Mes})]^+$ fragment analogous to lighter homologs^[2]
- Good correspondence of the experimental and calculated Pb—Pb and Cu—C bond distances
- Shortening of the calculated Pb—Cu distances can be attributed to the approximation of the NHC ligand as imidazole-2-ylidene, therefore reducing steric hindrance towards the lead cage
- The plumbide cage can be described as a monocapped square antiprism with near C_{4v} symmetry, based on a diagonal ratio of $d(Pb1-Pb3)/d(Pb2-Pb4) = 1.06$ or 1.00 for the experimental and calculated cluster respectively



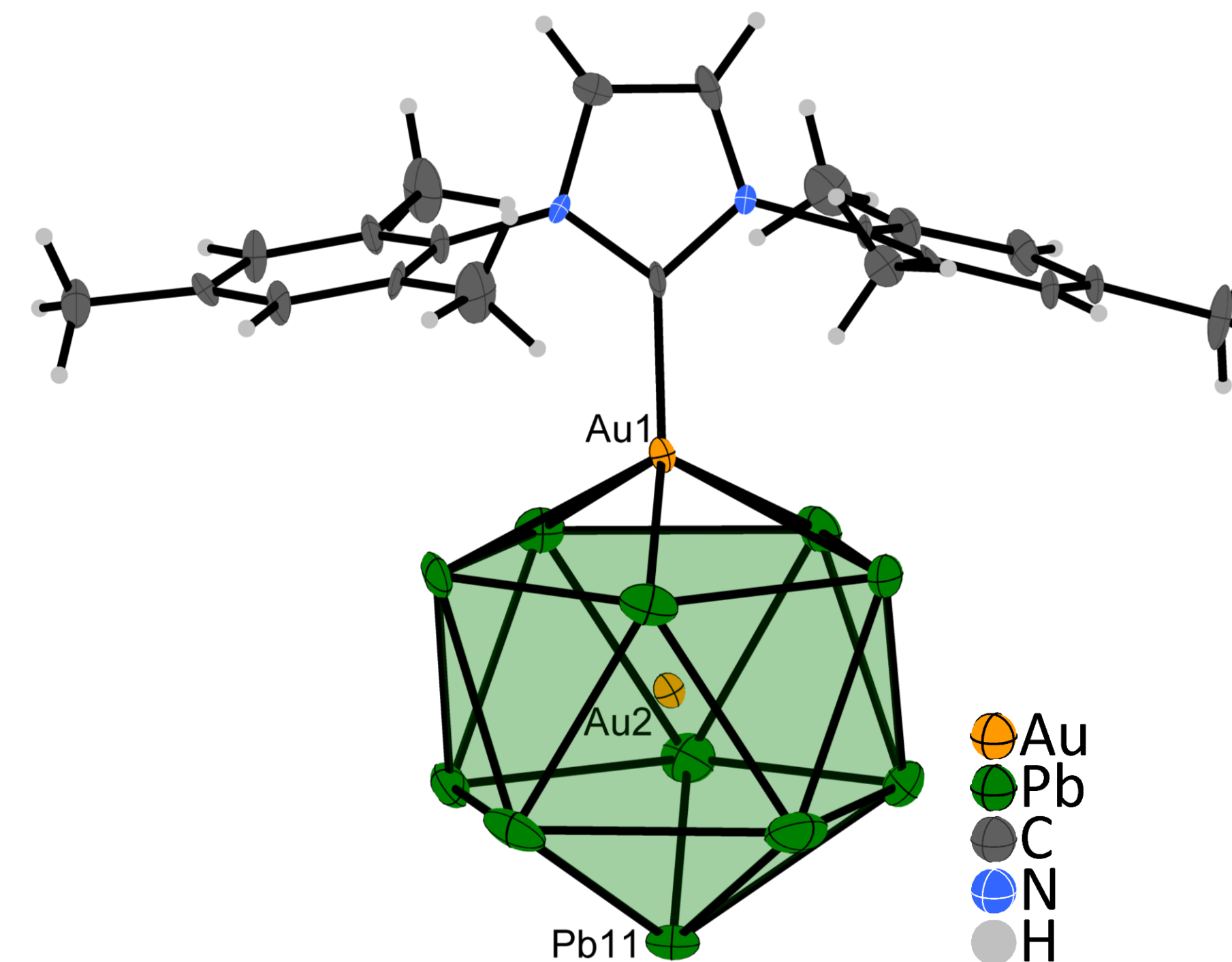
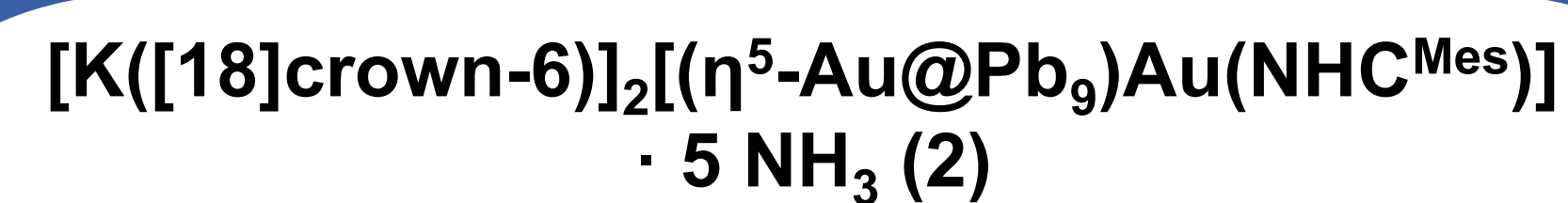
Synthesis:

$K_4Pb_9 + NHC^{Mes}MCl$ (M = Cu (1), Au (2)) + 2.5 [18]crown-6 + 1.5 [2.2.2]cryptand (for (1) only)
The reactants are dissolved in liquid ammonia and stored at -40 °C. After 9 months (1) or 7 months (2) black, needle like crystals are obtained.

X-Ray

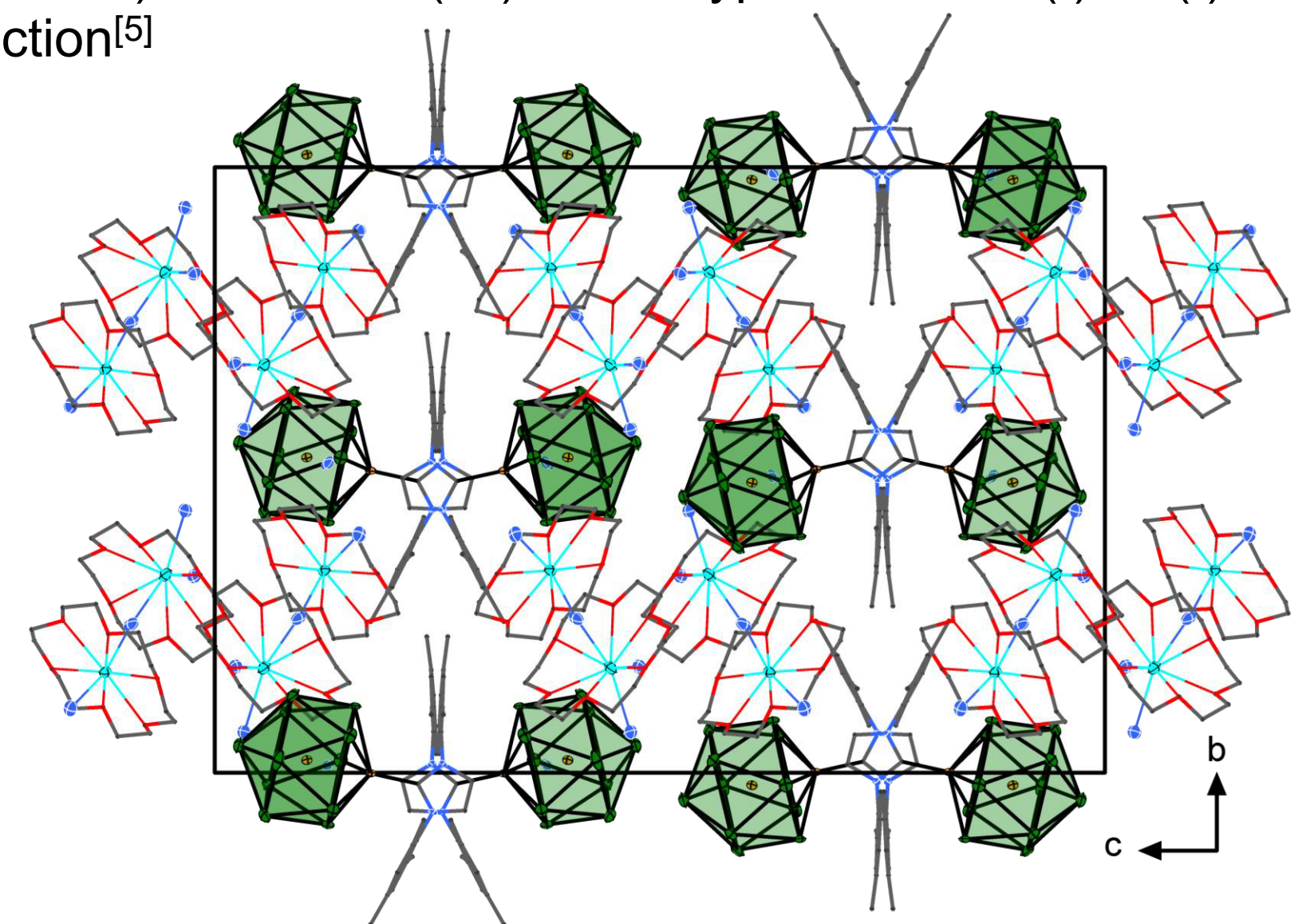


DFT

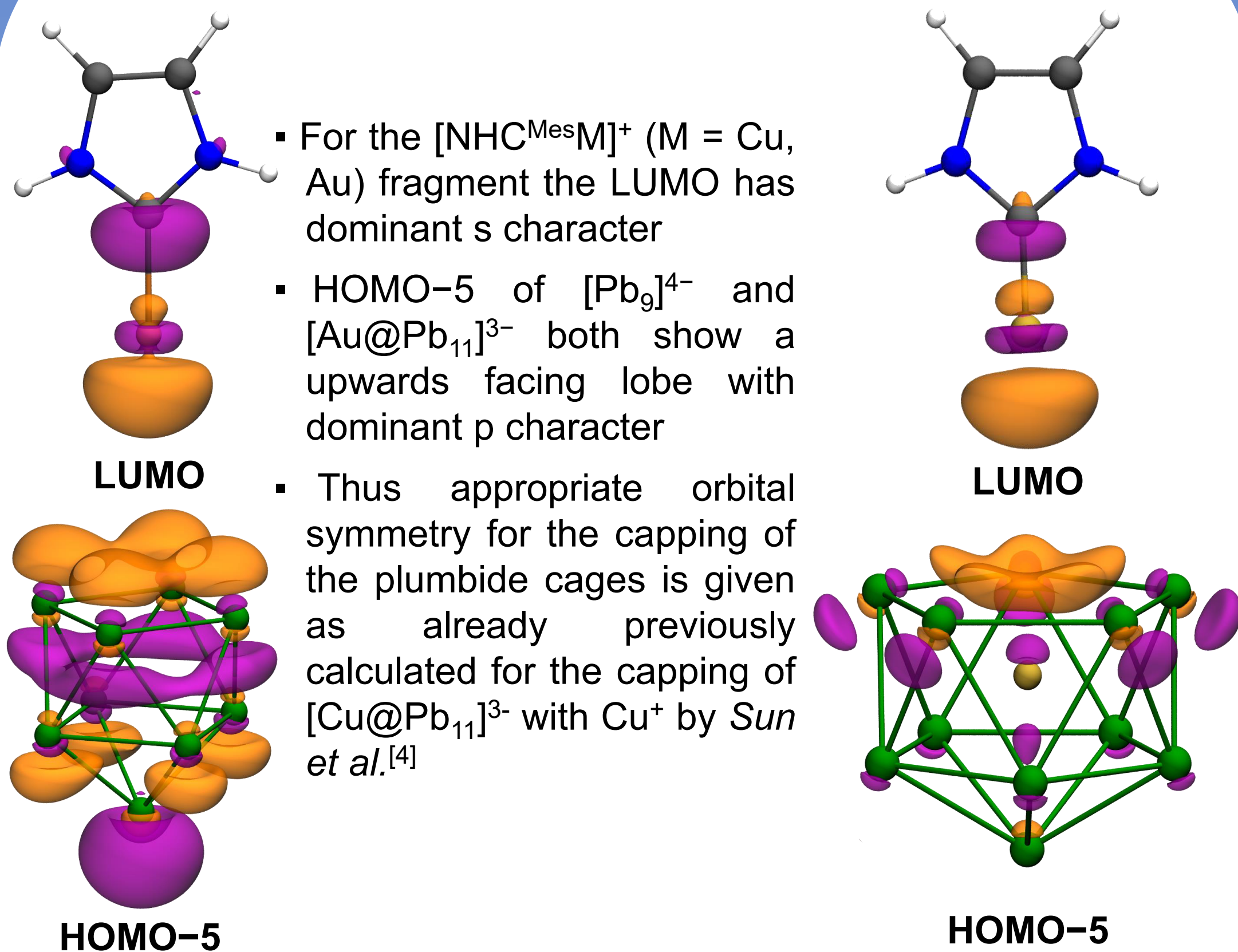


	d_{exp} [Å]	d_{calc} [Å]
d(Pb—Pb)	3.1900(8) – 3.2303(11)	3.136 – 3.176
d(Pb—Au1)	2.9640(7) – 3.0218(8)	2.965 – 3.004
d(Pb—Au2)	2.9474(11) – 3.1269(9)	2.990 – 3.011
d(Au1—C)	2.037(11)	1.656
d(Au1—Au2)	2.7548(11)	2.5738

- Rearrangement of $[Pb_9]^{4-}$ in solution in the presence of Au^+ to the endohedral species $[Au@Pb_{11}]^{3-}$ followed by capping of the pentagonal face as calculated for a similar system containing Cu^+ by Sun *et al.*^[4]
- Good correspondence of the experimental and calculated Pb—Pb and Pb—Au1 bond distances
- Differences in the Pb—Au2 distances can be attributed to optimized centering of Au2 in the calculated structure, whereas a shortened Au1—C and Au1—Au2 distance results from approximating the NHC ligand as imidazole-2-ylidene
- d(Au1—Au2) of 2.7548(11) Å is typical for Au(I)—Au(I) aurophilic interaction^[5]



Illustrating the Capping Using Kohn-Sham Orbitals

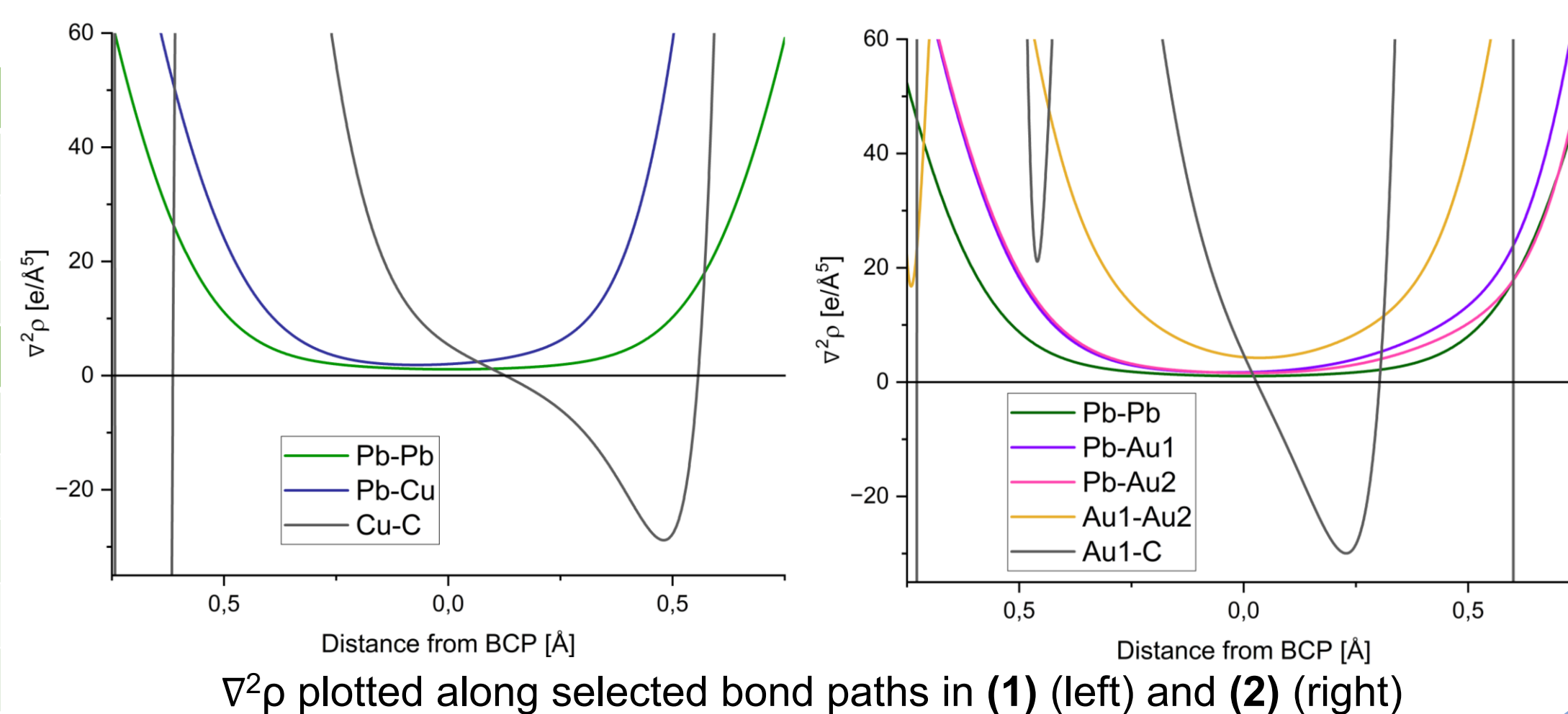


All DFT calculations were carried out using B3LYP/jeorge-TZP-DKH levels of theory as well as implementing a CPCM model with ammonia as the solvent. NHC ligands were approximated as imidazole-2-ylidene.

Classification of the Bonding Situation

- The bonding situation can be classified by examining bond descriptors at the bond critical points (BCP) according to Bianchi *et al.*^[6]
- Pb—Pb interactions in both (1) and (2) show low electron density ρ_b , a positive Laplacian of the electron density $\nabla^2\rho_b$ as well as a negative virial potential energy density V_b at the BCP indicating typical M—M bonding interaction
- The same is true for other Pb—M interactions, however slight polarization can be observed, when plotting $\nabla^2\rho$ along the bond path
- Charge accumulation, indicated by a negative $\nabla^2\rho$, is only present along the M—C bond paths, which can be interpreted as the carbene lone pair donating electrons to the metal center
- Therefore, the plumbide cages should not be considered classical electron donor ligands but rather as integrating the coinage metal into the cluster structure

	ρ_b [e/Å ³]	$\nabla^2\rho_b$ [e/Å ⁵]	V [H/Å ³]
(1)			
Pb—Pb	0.210	0.991	-0.121
Pb—Cu	0.318	2.040	-0.270
Cu—C	0.765	7.990	-1.240
(2)			
Pb—Pb	0.200	1.050	-0.115
Pb—Au1	0.240	1.650	-0.175
Pb—Au2	0.237	1.570	-0.169
Au1—Au2	0.487	4.360	-0.525
Au1—C	2.030	4.700	-4.450



[1] E. Zintl, J. Goubeau, W. Dullenkopf, *Z. Phys. Chem. A* 1931, 1–46.

[2] C. Liu, Z. M. Sun, *Coord. Chem. Rev.* 2019, 382, 32–56.

[3] S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed.* 2011, 50, 3630–3670.

[4] H. W. T. Morgan, C. C. Shu, Z. M. Sun, J. E. McGrady, Z. M. Sun, *J. Am. Chem. Soc.* 2022, 142, 8007–8017.

[5] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* 2011, 41, 270–412.

[6] R. Bianchi, G. Gervasio, D. Marabello, *Inorg. Chem.* 2000, 39, 2360–2366.