

Is CLi₆ hypervalent?

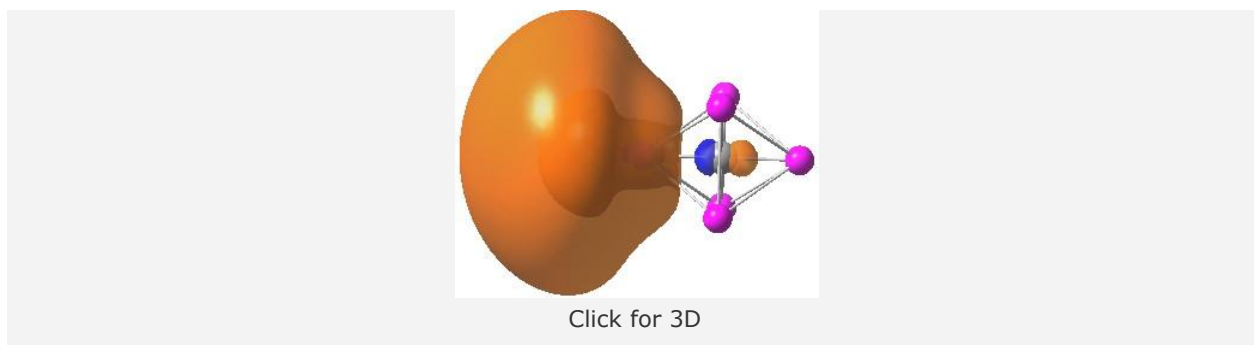
A [comment](#) made on the previous post on the topic of hexa-coordinate carbon cited an article entitled "*Observation of hypervalent CLi₆ by Knudsen-effusion mass spectrometry*"[\[1\]](#) by Kudo as a amongst the earliest of evidence that such species can exist (in the gas phase). It was a spectacular vindication of the earlier theoretical prediction[\[2\],\[3\]](#) that such 6-coordinate species are stable with respect to dissociation to CLi₄ and Li₂.

The terminology describes these lithium carbides as effectively **hypervalent**; Kudo in the abstract of his 1992 article uses the more explicit phrase "*carbon can expand its octet of electrons to form this relatively stable molecule*". We are taught early on in chemistry that the carbon octet is due to double occupation of four molecular orbitals formed using linear combinations derived from the relatively low energy 2s/2p carbon atomic orbital basis. Octet expansion on carbon must therefore involve to some degree the next atomic shell (3s/3p), which is normally regarded as too high in energy to be capable of significant population for carbon. But use of the 3s/3p shell seems at first sight inevitable. If one constructs an octahedral complex CLi₆ surely ten electrons must be involved in bonding, four from the carbon and six from the equivalent lithiums? The 3s/3p carbon population must therefore be ~2 electrons, and we can truly describe a molecule where carbon has of necessity expanded its octet of electrons to ten as hypervalent. Or can we?

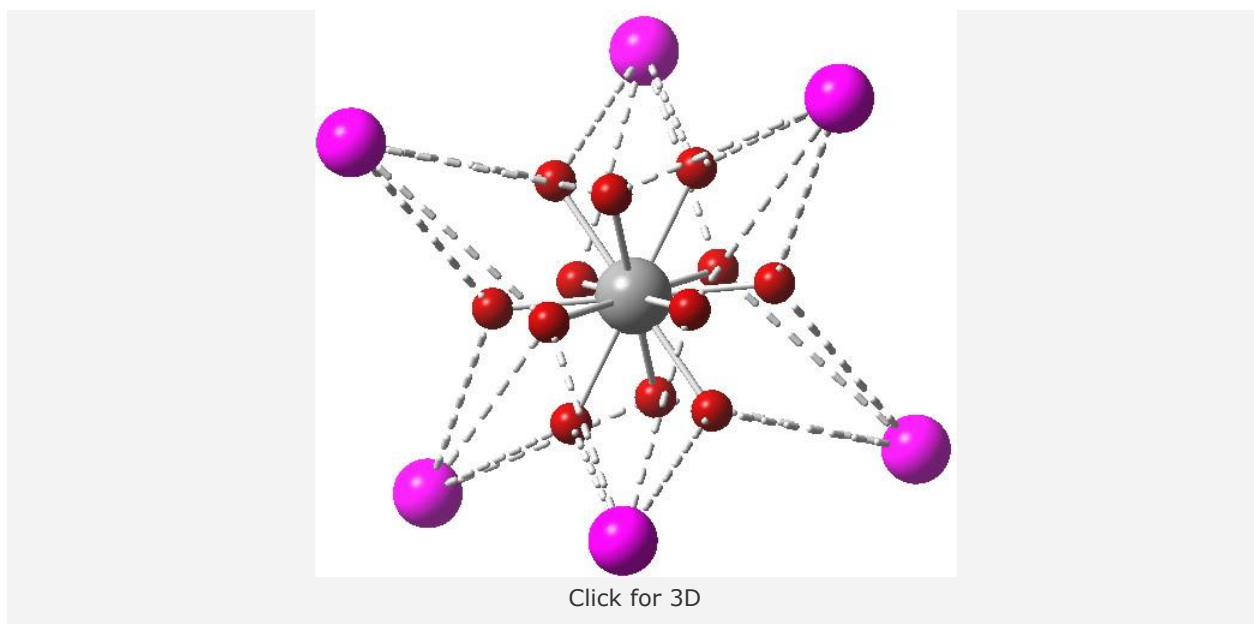
How does a quantitative (ω B97XD/6-311++G(d)) calculation[\[4\]](#) reveal this effective hypervalency?

1. The octahedral geometry is indeed a stable minimum, with the lowest vibrational wavenumber being 194 cm⁻¹.
2. It also checks out as clearly a closed shell species, stable to open shell perturbations.
3. An NBO analysis reveals the Rydberg population (those 3s/3p atomic orbitals) to be only 0.09 electrons.
4. It partitions the electrons into 13.97 for the 1s cores of the seven atoms, 7.67 "valence-Lewis" (i.e. shared covalent) and a mysterious 2.27 (valence, non-Lewis).

We now have a problem. One of the standard methods for partitioning electrons has isolated two of our ten electrons and placed them, with small partial occupancy, into unshared "lone pairs", located as it happens on the lithium atoms (shown below for one of these partial lone "pairs"). The carbon is NOT hypervalent, and it has NOT expanded its octet.



So I tried another procedure, deliberately chosen to be rather different from the orbital-based NBO formalism. This is analysis of the ELF, or electron localisation function, and represents an attempt to derive the result based on a function related to the electron density. The red spheres shown below are the centroids of the **twelve** ELF basins located:



Each of these (equivalent) basins has an electron population of ~ 0.81 , making ~ 9.7 electrons in total. Each lithium sits on a square arrangement of four of these basins, and so has access to ~ 3.2 valence electrons. How do we interpret the situation for carbon however? Does its valence shell contain an expanded 9.7 electrons? Well, not necessarily. You can see that each of the basins has a three-centre relationship between the one

carbon and TWO lithiums. These electrons contribute not just to C-Li bonding, but also to Li...Li bonding. So these 9.7 electrons contribute in part to bonding that does NOT involve the carbon. We can see this in the (Wiberg) bond orders, 0.254 for the C-Li interaction, and 0.116 for adjacent Li...Li interactions (such an explanation was also **suggested** for why II_7 has no expanded octet at the central iodine). In fact, the origins of this effect were first clearly identified in the theoretical analysis of 1983[3]: *"the extra electrons beyond the usual octet are involved with metal-metal bonding rather than with interactions of the metals with the central atoms"*.

It is nice to see that despite the passage of 30 years, and despite the introduction of many new ways of analysing the wavefunctions and hence the bonding of molecules, the essential original interpretation[3] remains robustly correct!

Source: <http://www.ch.imperial.ac.uk/rzepa/blog/?p=10801>