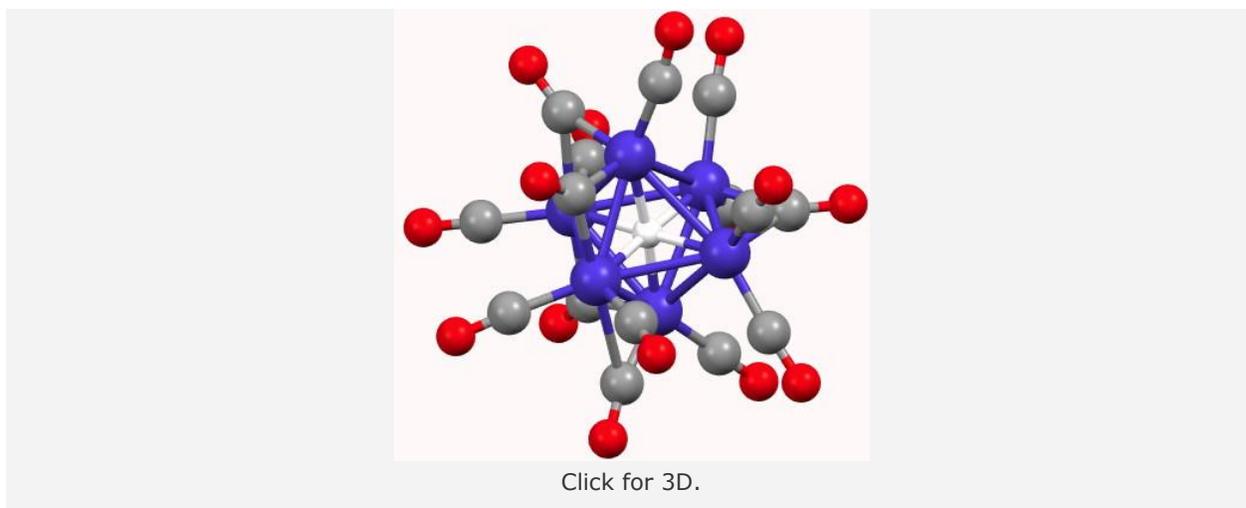


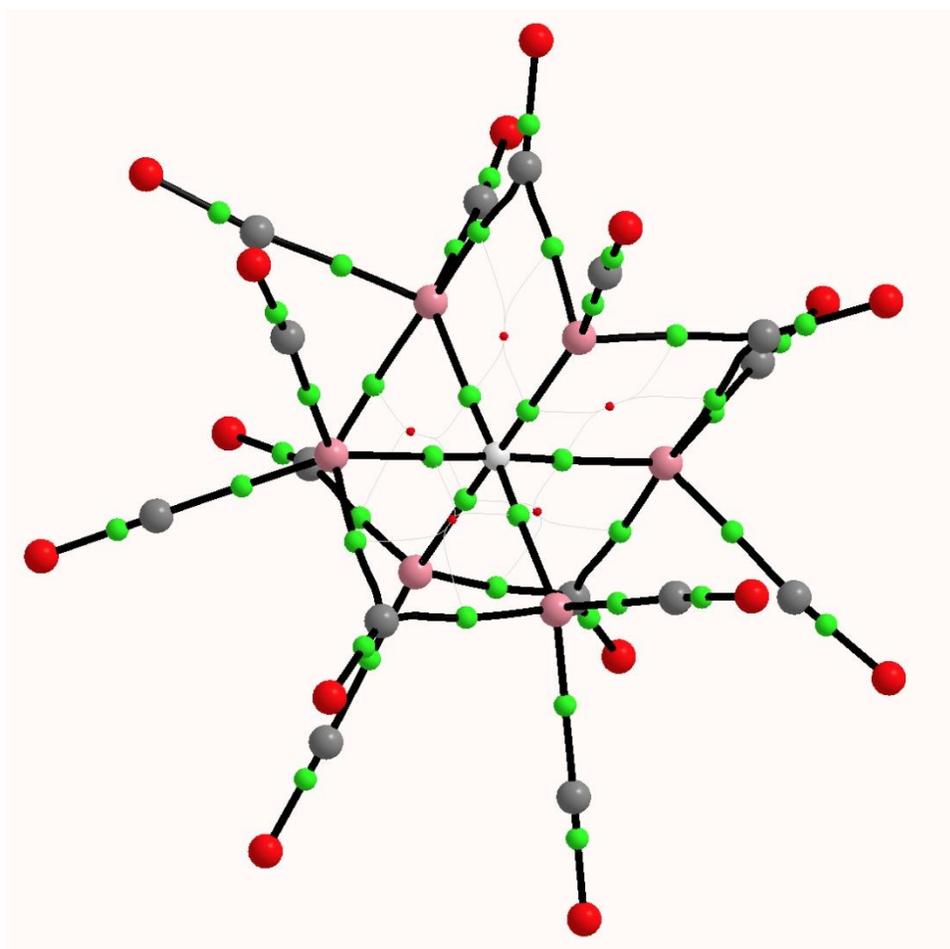
Hexacoordinate hydrogen

A feature of a blog which is quite different from a journal article is how rapidly a topic might evolve. Thus I started a few days ago with the theme of dicarbon (C_2), identifying a metal carbide that showed C_2 as a ligand, but which also entrapped a single carbon in hexa-coordinated mode. A comment was posted bringing attention to the origins of the discovery of hexacoordinated carbon, and we moved on to exploring the valency in one such species (CLi_6). Here I ask if hydrogen itself might exhibit such coordination.



In fact, such a system was first reported as long ago as 1981[1]. This contains a cobalt carbonyl anion of the type $[Co_6H(CO)_{15}]^-$. The hexacoordinated hydrogen had a measured 1H NMR chemical shift of 23.2 ppm (very low field), a value normally more associated with a proton rather than a hydride.

What does quantum mechanics say about this system? The QTAIM ($\omega B97XD/6=311G(d,p)$) calculation[2] is shown below. The green spheres represent bond critical points, and indeed six surround the central hydrogen with octahedral coordination. The value of $\rho(r)$ for these varies from 0.074 to 0.082 au, which is a higher electron density than might be found for *e.g.* a hydrogen bond (which is typically 0.020 – 0.010 au). The individual $Co...H$ Wiberg bond order indices are ~ 0.1 (the total Wiberg bond index is 0.86).



The computed ^1H chemical shift[3] (relative to TMS) of the hydrogen is 30.8 ppm, which seems to agree with an interpretation based on a proton in the interstitial cavity. However, the NBO natural charge on this hydrogen is -0.41, for a valence population of 1.40 electrons (and a Rydberg population of 0.01), which makes it more of a hydride anion than a cationic proton. NBO characterises this electron population as “Lp” (Lone pair). One might conclude from these apparently opposed indications that the deshielding of the ^1H is less to do with its resemblance to a proton, and is more due to the local magnetic currents originating from the metal atoms.

It is still nicely surprising that even an element as small as hydrogen can sustain hexa-coordination. It also reminds that although each of the coordinations is *via* what can reasonably be called a bond, the hydrogen nevertheless does not exceed its maximum valence electron shell electron count of two; in that sense it is not hypervalent.

References

1. D.W. Hart, R.G. Teller, C. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, and T.F. Koetzle, "An interstitial hydrogen atom in a hexanuclear metal cluster: x-ray and neutron diffraction analysis of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{HCo}_6(\text{CO})_{15}]^-$ ", J. Am. Chem. Soc., vol. 103, pp. 1458-1466, 1981.<http://dx.doi.org/10.1021/ja00396a028>
2. Henry S. Rzepa., "Gaussian Job Archive for $\text{C}_{15}\text{HCo}_6\text{O}_{15}(1^-)$ ", 2013. <http://dx.doi.org/10.6084/m9.figshare.741232>
3. H.S. Rzepa, " $\text{C}_{15}\text{H}_1\text{Co}_6\text{O}_{15}^-$ ", 2013.<http://hdl.handle.net/10042/24804>

Source: <http://www.ch.imperial.ac.uk/rzepa/blog/?p=10839>