Molecular structures of 1,12-$B_{12}H_{10}(CO)_2$ and its dihydrate 1,12-$B_{12}H_{10}[C(OH)_2]_2$

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1,12-$B_{12}H_{10}(CO)_2$

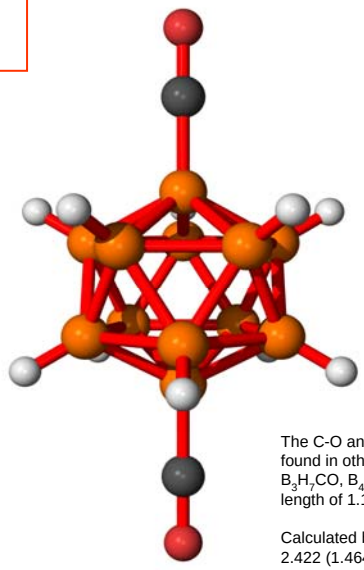
Dodecaborane dicarbonyl 1,12-$B_{12}H_{10}(CO)_2$ is made via several steps starting from the *closo*-borane dianion $B_{12}H_{12}^{2-}$ and carbon monoxide CO with catalyst at 130ºC and 1000 atm for 3 hours.

$$(H_3O)_2B_{12}H_{12} + CO \rightarrow \rightarrow \rightarrow 1,12\text{-}B_{12}H_{10}(CO)_2$$
catalyst $Co_2(CO)_8$

$B_{12}H_{12}^{2-}$ has a regular icosahedron geometry and is the most aromatic of all *closo* borane dianions, $B_nH_n^{2-}$. In metal carbonyls the π bonding in the metal-carbon bond is substantial. We are interested in interactions between the substituted carbonyl groups and the borane cage.

Fragile crystals were grown by slow sublimation under high vacuum at 40ºC for 2-4 days. A crystal of the dicarbonyl $B_{12}H_{10}(CO)_2$ was flash-frozen to 100 K and an X-ray diffraction study revealed a well ordered discrete structure of high symmetry (only nine atoms unique).

This is the first neutral *closo* borane carbonyl to be structurally characterized.

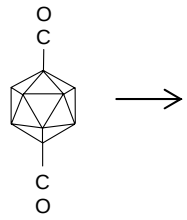


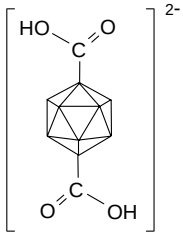
The C-O and B-C bond lengthsare typically found in other borane carbonyls; BH_3CO, B_3H_7CO, B_4H_8CO. Free CO has a bond length of 1.128 Å.

Calculated bond orders (π in brackets) are 2.422 (1.464) for CO and 0.843 (0.114) for B-C. There is small π-bond interaction between the cage and the CO group.

1,12-$B_{12}H_{10}[C(OH)_2]_2$

Reported:

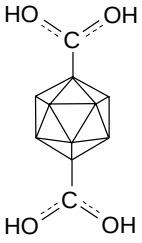




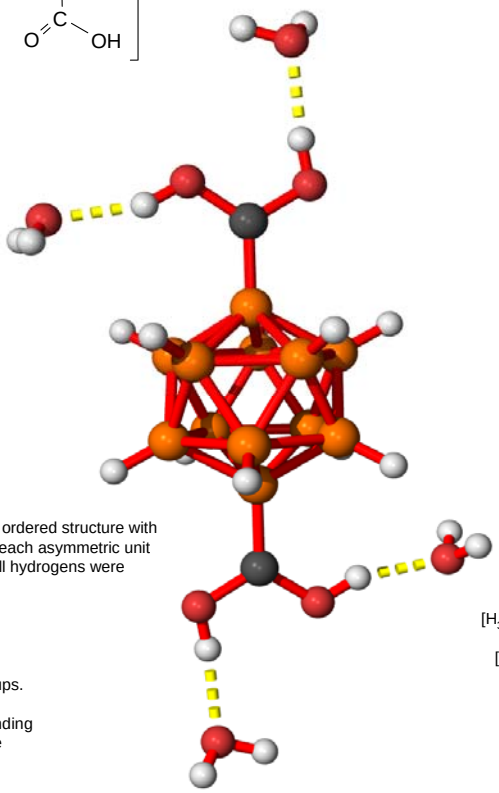
2 H_3O^+

x H_2O

It is in fact



4 H_2O

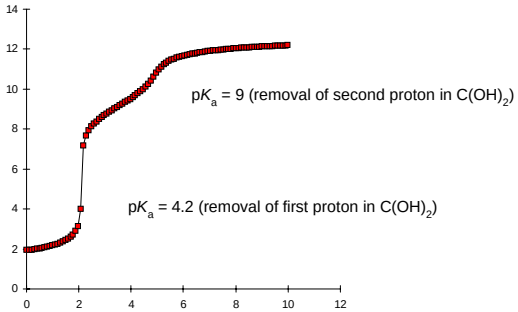


A crystal of the hydrate shows a well ordered structure with two independent water molecules in each asymmetric unit by an X-ray diffraction study where all hydrogens were refined freely.

It is the first structurally characterized compound with two carbene diol groups.

There is intermolecular hydrogen bonding between the water molecules and the borane molecules.

Preliminary Titration of $B_{12}H_{10}[C(OH)_2]_2$



Distances for the two unique C-O bonds are 1.287Å and 1.289 and for B-C 1.589.

Calculated bond orders (π in brackets) are 1.30 (0.390) for C-O and 0.83 (0.064) for B-C.

So the C-O bonds contain substantial π bonding and the B-C bond has negligible π bonding.

Future work

Other reported borane carboxylic acids

$[H_3O^+]_2[1,10\text{-}B_{10}H_8(CO_2H)_2^{2-}]$ $[H_3O^+]_2[1,7\text{-}B_{12}H_{10}(CO_2H)_2^{2-}]$

$[H_3O^+]_2[2\text{-}B_{10}H_9(CO_2H)^{2-}]$ $[H_3O^+]_2[B_{12}H_{11}(CO_2H)^{2-}]$

Could they contain $C(OH)_2$ instead of CO_2H groups?

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