Chapter 10

Hydrogen

Hydrogen and hydride ions

Isotopes of hydrogen

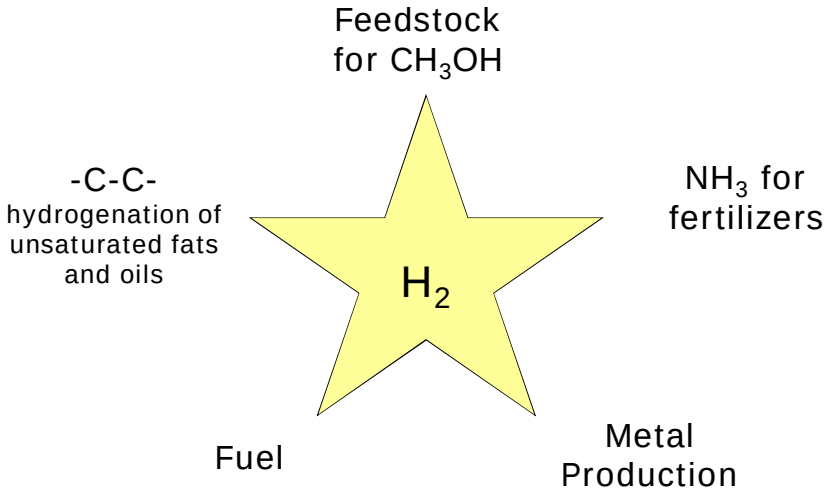
Dihydrogen

Polar and non-polar E-H bonds

Hydrogen Bonding

Classes of binary hydrides

Major Uses of Hydrogen



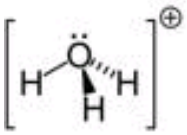
Water of crystallization

- Solids that consist of molecules of a compound along with water molecules are named hydrates.
- Contain water bound to cations to anions or other electron rich atoms via hydrogen bonds.
  - $[M(OH_2)_6]^{n+}$ etc.
- Water of crystallization found in some crystals and hydrated metal halides e.g. $CuSO_4.5H_2O$
- $CoCl_2(H_2O)_6$ has a coordination sphere around the metal as *trans*-$[CoCl_2(H_2O)_4]$ and two equivalents of water of crystallization that are not bound to Co.

Hydrated Protons

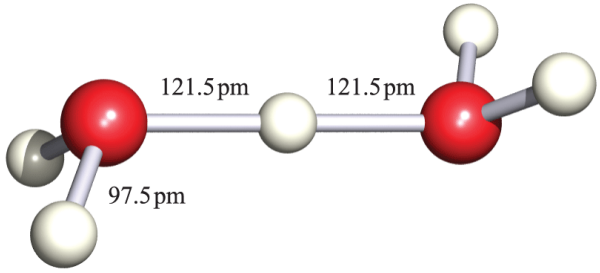
$H(g) \rightarrow H^+(g) + e^-$ Ionization Energy 1312 kJ mol^{-1}

$[H_3O]^+$ is the hydrated proton or oxonium ion



- $\Delta_{hyd}H^o(H^+, g) = 1091$ kJ mol^{-1}

$[H_5O_2]^+$

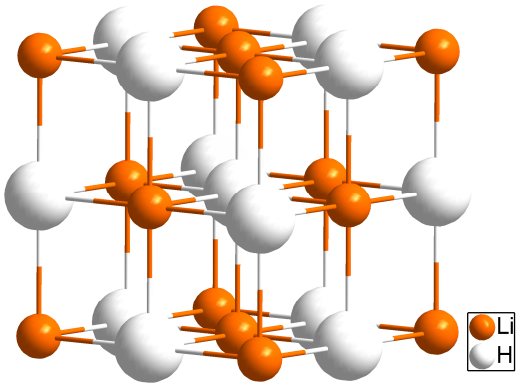


Hydride Ion

$H(g) + e^- \rightarrow H^-(g)$ $\Delta_{EA}H(298K) = -73\ kJ\ mol^{-1}$

In the solid state, all alkali metal hydrides crystallize with the NaCl structure type.

•From the crystal structure, the radius of H^- can be estimated by: internuclear distance = $r_{cation} + r_{anion}$



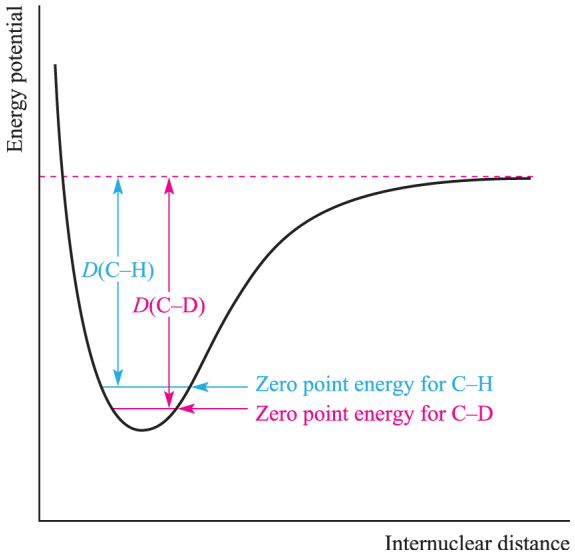
Isotopes of Hydrogen

Three common isotopes: protium, deuterium, and tritium

	Protium	Deuterium	Tritium
Symbols†	^{1}H or H	^{2}H or D	^{3}H or T
Natural abundance	99.985%	0.0156%	<1 in 10^{17} atoms
Isotopic mass / u	1.0078	2.0141	3.0160
Nuclear spin	$\frac{1}{2}$	1	$\frac{1}{2}$

† Strictly, ^{1}H should be written as $^1_1$H, ^{2}H as $^2_1$H and ^{3}H as $^3_1$H, but the less rigorous symbols are generally used.

Kinetic Isotope Effect



The zero point energy (corresponding to the lowest vibrational state) of a C–D bond is lower than that of a C–H bond and this results in the bond dissociation enthalpy, *D*, of the C–D bond being greater than that of the C–H bond.

Selected properties of H_2O and D_2O ('heavy water').

Property	H_2O	D_2O
Melting point / K	273.00	276.83
Boiling point / K	373.00	374.42
Temperature of maximum density / K[†]	277.0	284.2
Maximum density / g cm^{-3}	0.999 95	1.105 3
Relative permittivity (at 298 K)	78.39	78.06
K_w (at 298 K)	1×10^{-14}	2×10^{-15}
Symmetric stretch,[‡] $\tilde{\nu}_1$ (gaseous molecule) / cm^{-1}	3657	2671

[†] See Fig. 7.2.
[‡] The symmetric stretching mode is illustrated (for SO_2) in Fig. 3.12.

Why is the boiling point of D_2O greater than that of H_2O?

What about tritium? Where does it come from?

Dihydrogen

Physical property	Value
Melting point / K	13.66
Boiling point / K	20.13
Enthalpy of vaporization / kJ mol^{-1}	0.904
Enthalpy of fusion / kJ mol^{-1}	0.117
Density (273 K) / g dm^{-3}	0.090
Bond dissociation enthalpy / kJ mol^{-1}	435.99
Interatomic distance / pm	74.14
Standard entropy (298 K) / J K^{-1} mol^{-1}	130.7

Selected physical properties of H_2.

Dihydrogen production

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

$2Al(s) + 2NaOH(aq) + 6\ H_2O(l) \rightarrow 2Na[Al(OH)_4](aq) + 3\ H_2(g)$

$CaH_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + 2H_2(g)$

$$CO + 2H_2 \xrightarrow[\sim 550\ K,\ 50\ bar]{Cu/ZnO\ catalyst} CH_3OH$$

Haber Process

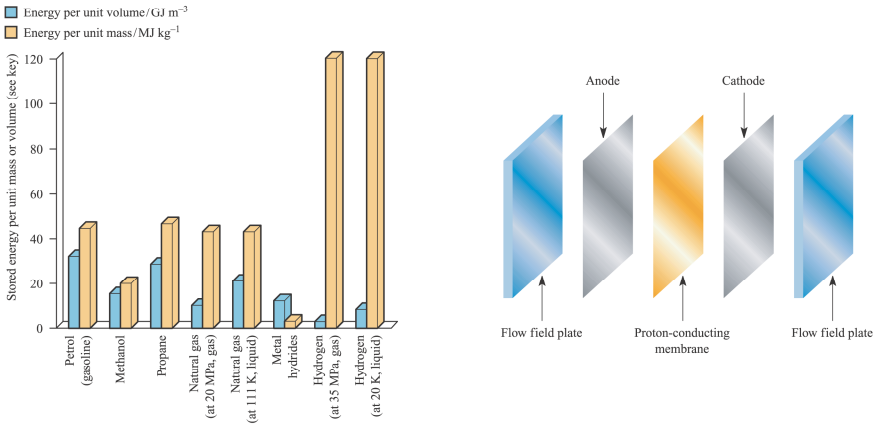
Reagents above are known as **synthesis gas**. and the mixture is manufactured by the **water-gas shift** reaction.

$$CH_4 + H_2O \xrightarrow[\sim 1200\ K]{Ni\ catalyst} CO + 3H_2$$

$$CO + H_2O \xrightarrow[\sim 700\ K]{iron\ oxide\ catalyst} CO_2 + H_2$$

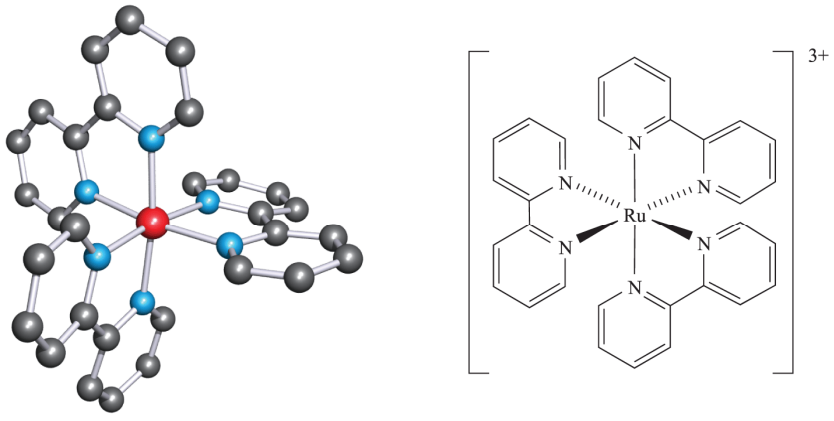
hydrogen economy – formation of H_2 from H_2O requires a large energy input

Hydrogen Economy



Box 10.2 Left: Stored energy in various fuels. Right: The assembly of one cell in a polymer electrolyte membrane fuel cell.

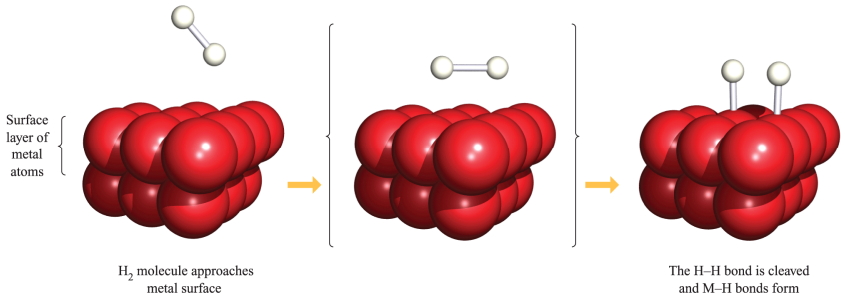
Photocatalyst



(a) (b)

$[Ru(bpy)_3]^{3+}$ (bpy = 2,2'-bipyridine)

Reactivity



Interaction of an H_2 molecule with a metal surface to give *adsorbed* hydrogen atoms

Polar and non-polar bonds

$\delta^+ \quad \delta^-$
E — H

$\chi^P(H) > \chi^P(E)$

$\delta^- \quad \delta^+$
E — H

$\chi^P(H) < \chi^P(E)$

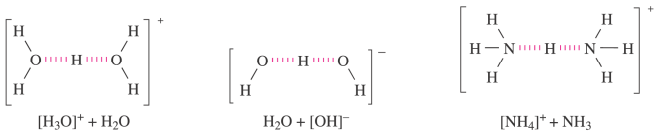
The direction of the dipole moment in a polar E–H bond depends upon the relative electronegativity values.

- The direction in which the arrow points ($\delta-$ to $\delta+$) is defined by SI convention.

The difference in electronegativity values between E and H means the bond may be:

- Non-polar, or polar in either of the senses given the diagram above.
- When E is a p-block element, B-H, C-H, Si-H bonds are essentially non-polar
- When E is a metal (electropositive) H carries a partial negative charge.
- When E is N, O, or F the H atom carries a partial positive charge

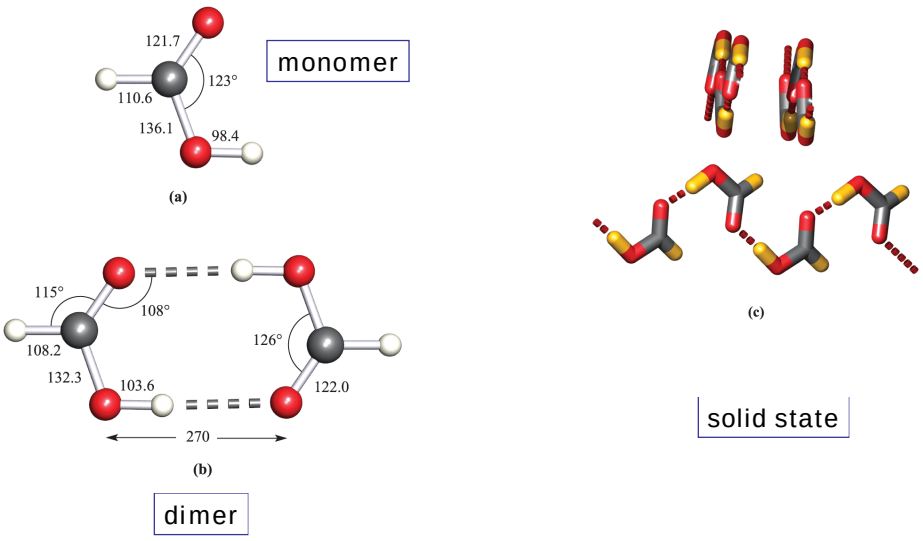
Hydrogen bonding



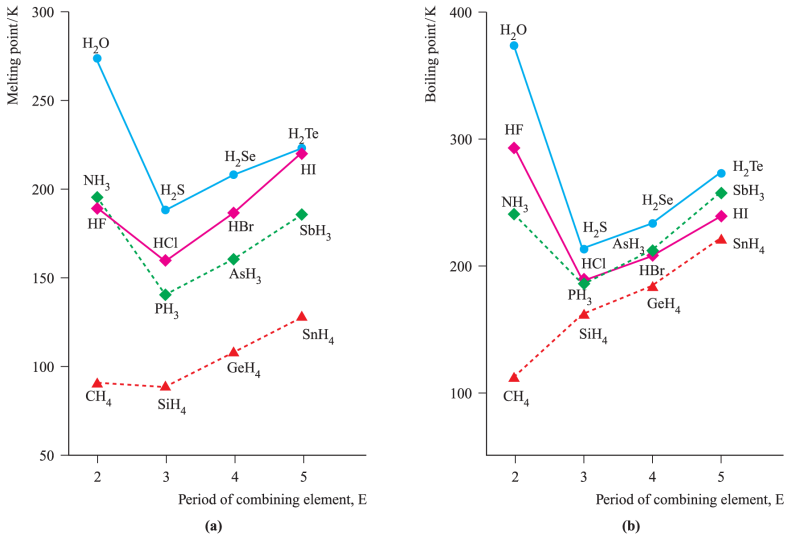
Category of hydrogen bond	Hydrogen bond (····)	Dissociation enthalpy / kJ mol^{-1}
Symmetrical	F····H····F in $[HF_2]^-$ (see eq. 10.26)	163
Symmetrical	O····H····O in $[H_5O_2]^+$ (see structure **10.2**)	138
Symmetrical	N····H····N in $[N_2H_7]^+$ (see structure **10.4**)	100
Symmetrical	O····H····O in $[H_3O_2]^-$ (see structure **10.3**)	96
Asymmetrical	N–H····O in $[NH_4]^+$····OH_2	80
Asymmetrical	O–H····Cl in OH_2····Cl^-	56
Asymmetrical	O–H····O in OH_2····OH_2	20
Asymmetrical	S–H····S in SH_2····SH_2	5
Asymmetrical	C–H····O in HC≡CH····OH_2	9
Asymmetrical	C–H····O in CH_4····OH_2	1 to 3

† Data are taken from: T. Steiner (2002) *Angew. Chem. Int. Ed.*, vol. 41, p. 48.

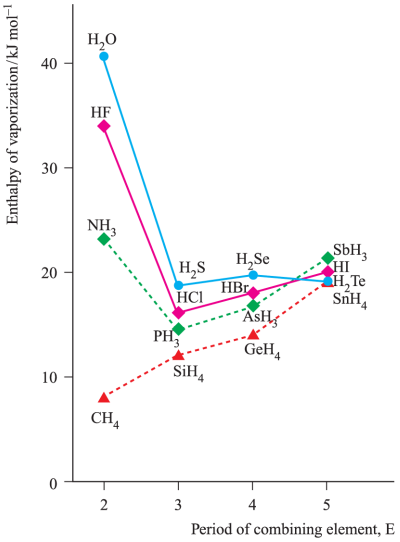
Hydrogen bonding in formic acid



Trends in (a) melting and (b) boiling points for some *p*-block hydrides, EH_n.



$\Delta_{vap}H$ (measured at the boiling point of the liquid) for some *p*-block hydrides, EH_n.



Trouton's Rule

An interesting and useful approximation:

• The ratio of the heat of vaporization and the boiling point is (approximately) constant

$\Delta_{vap}S = \Delta_{vap}H/bp \sim 88\ J\ K^{-1}\ mol^{-1}$

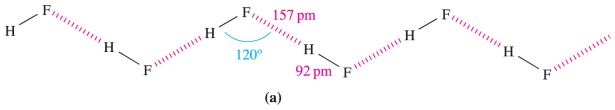
• Boiling point of cyclohexane is 69°C. Therefore,

$\Delta_{vap}H = (69 + 273)(88) \sim 30\ kJ/mol$

which is within 2-3% of the experimental value

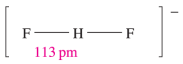
• Works well for unassociated liquids and gives useful information about degree of association.

Solid state structure of HF



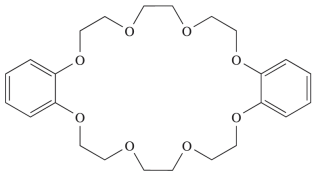
(a)

$[HF_2]^-$ ion

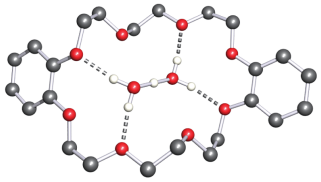


(b)

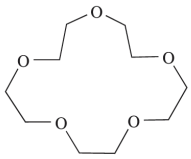
stabilization in the solid state of $[H_5O_2]^+$ and $[H_7O_3]^+$ by hydrogen bonding to crown ethers



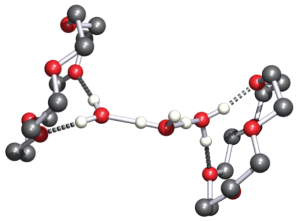
(a)



(b)

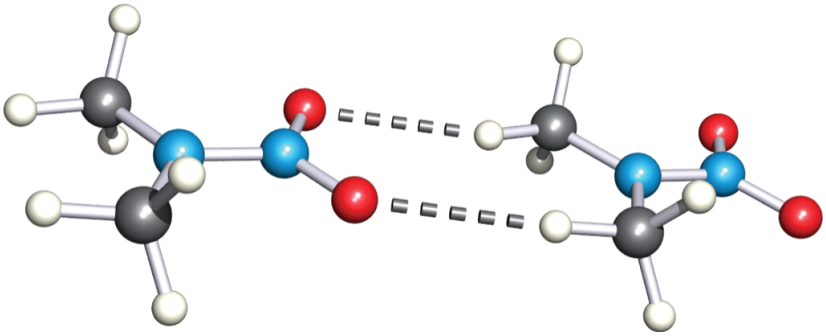


(c)

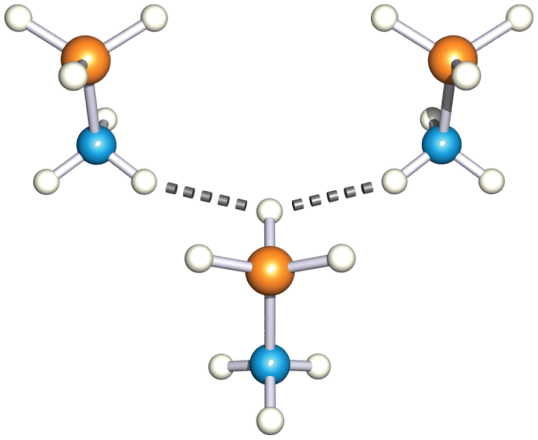


(d)

Hydrogen-bonded chains in the solid-state structure of Me_2NNO_2



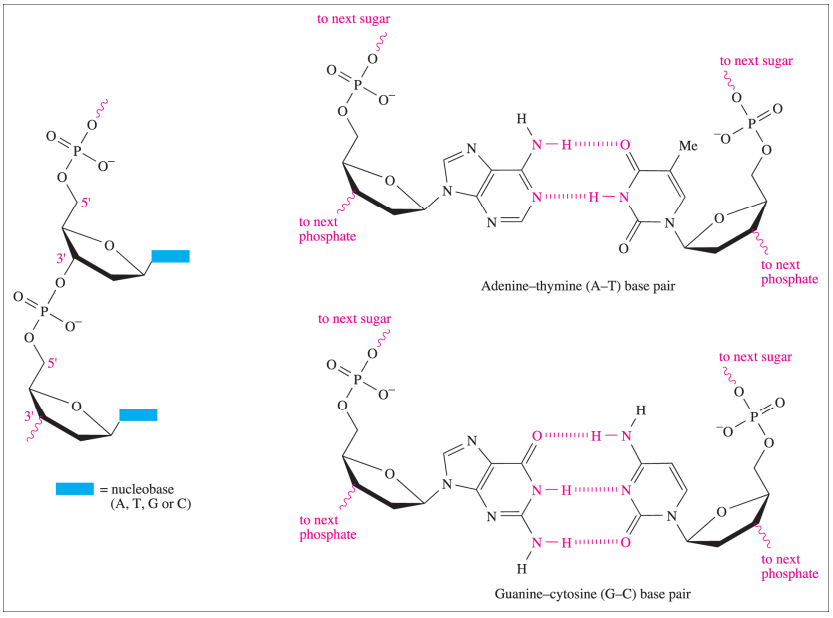
Dihydrogen Bond



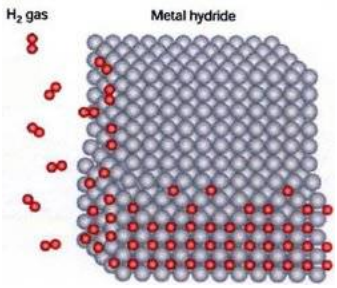
1 H 2.20																	
3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98	
11	12											13	14	15	16	17	

Pauling Electronegativity Values

Hydrogen bonding in biological systems



Binary Hydrides

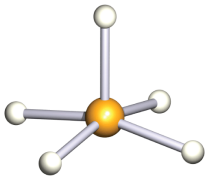


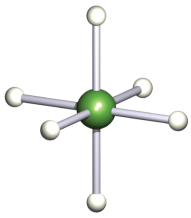
Four major classes: metallic, saline (salt like), molecular, covalent (with extended structures)

Metal	$\Delta_a H^o$(M) / kJ mol^{-1}	IE_1(M) / kJ mol^{-1}	$\Delta_{lattice} H^o$ / kJ mol^{-1}	$\Delta_f H^o$(MH) / kJ mol^{-1}
Li	161	521	−920	−90.5
Na	108	492	−808	−56.3
K	90	415	−714	−57.7
Rb	82	405	−685	−52.3
Cs	78	376	−644	−54.2

Molecular hydrido complexes

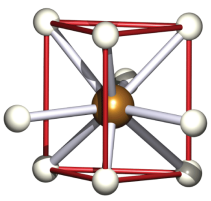
$[CoH_5]^{4-}$

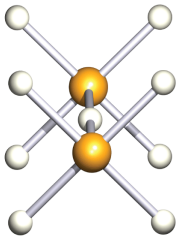




$[FeH_6]^{4-}$

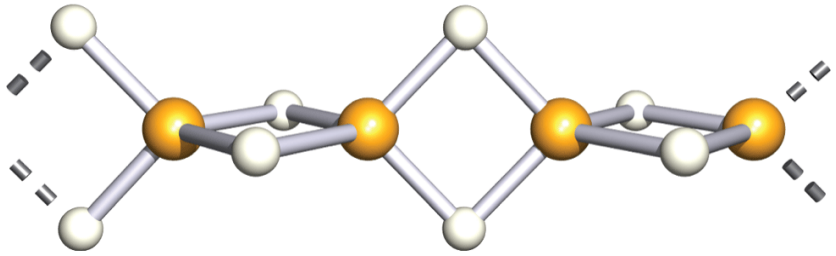
$[ReH_9]^{2-}$





$[Pt_2H_9]^{5-}$

Polymeric Hydrides



polymeric chain structure of BeH_2