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Complex Transition-Metal Hydrides

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Abstract. Complex transition-metal hydrides provide new opportunities for hydrogen storage. Their hydrogen-to-metal ratios reach values of up to $H/M = 4.5$ ($BaReH_9$) and thus surpass the hydrogen-to-carbon ratios of hydrocarbons (methane: $H/C = 4$); their hydrogen-volume efficiencies exceed that of liquid hydrogen by a factor of up to two (Mg_2FeH_6), their weight efficiencies exceed 5% (Mg_3MnH_7), and their hydrogen dissociation temperatures under 1 bar hydrogen pressure range from *ca.* 100° ($NaKReH_9$) to 400° ($CaMgNiH_4$). Their crystal chemistry is extremely rich and shows a large inventory of transition-metal hydrido complexes that often conform to the 18-electron rule. New synthetic methods are likely to yield further members of this class of materials.

1. History

Complex transition-metal hydrides constitute a relatively recent and somewhat exotic class of solid-state compounds. The historically first member and textbook example is K_2ReH_9 . It was reported in 1964 and found to contain tricapped trigonal prismatic $[Re^{VII}H_9]^{2-}$ complex anions in which rhenium is fully oxidised. The second member, Sr_2RuH_6 , was reported in the seventies and found to contain an octahedral $[Ru^{II}H_6]^{4-}$ complex. Wider interest in these compounds started only in the eighties after the discovery of typically metallic transition-metal hydrides, such as $LaNi_5H_6$ and $FeTiH_2$, which showed large homogeneity ranges with respect to hydrogen and turned out to be suitable media for reversible hydrogen storage [1]. One of these compounds, however, was nonmetallic (Mg_2NiH_4) and showed a nearly fixed hydrogen content. Originally reported in 1968, the compound was classified as a complex transition-metal hydride only 18 years later after its structure had been fully characterised and found to contain discrete tetrahedral $[Ni^0H_4]^{4-}$ complexes. This triggered an intense activity in the field and led to the discovery of many other homoleptic hydrido complexes, such as octahedral

$[FeH_6]^{4-}$, square-pyramidal $[CoH_5]^{4-}$, square-planar $[PtH_4]^{2-}$ and linear $[PdH_2]^{2-}$. Most of that work has been performed at the Universities of Geneva [2], Aachen [3] and Stockholm [4].

In 1994, some 25 complex ternary hydride structure types were known and have been reviewed [2]. Since then, their number

has increased at a steady rate and now totals over 40 structure types representing more than 70 ternary and quaternary metal hydrides. Most of them have hydrogen volume storage capacities that exceed that of liquid hydrogen, but are either too heavy, too expensive, or thermally too stable for reversible hydrogen storage applications at room temperature. The aim of current work is to find lighter and cheaper hydrides which decompose at or near ambient conditions, to develop new predictive concepts, to find new synthetic routes, and to understand the factors that govern hydride formation, hydrogen contents and thermal stability. In this article, some of that work is highlighted.

2. Current Work

2.1. Synthetic Routes

The presently known complex metal hydrides are based on late transition elements (group 7–10, including Cu and Zn), and monovalent or divalent metals (M) belonging to the alkali or alkaline-earth and lanthanide series, respectively. Most are true ternary (or quaternary) compounds in the sense that they do not derive from stable intermetallic compounds. They can be synthesised as polycrystalline materi-

Table 1. Complex Transition-Metal Hydrides^a): Hydride Anions and Hydrogen Storage Characteristics

Formula	Anions	Hydrogen wt. %	Density g/l	Desorption temperature at 1 bar	Ref.
$BaReH_9$	$[ReH_9]^{2-}$	2.7	134	<100°	[6a]
$NaKReH_9$	$[ReH_9]^{2-}$	3.5	117	<100°	[6b]
Mg_2FeH_6	$[FeH_6]^{4-}$	5.5	150	320°	[2]
Mg_3MnH_7	$[MnH_6]^{5-}, H^-$	5.2	119	>240°	[9]
$Ca_4Mg_4Fe_3H_{22}$	$[FeH_6]^{4-}, H^-$	5.0	122	395°	[2]
$SrMg_2FeH_8$	$[FeH_6]^{4-}, H^-$	4.0	115	440°	[8]
$LiMg_2RuH_7$	$[RuH_6]^{4-}, H^-$	4.3	113	>400°	[10a]
$LiMg_4Os_2H_{13}$	$[OsH_6]^{4-}, H^-$	2.6	121	>400°	[10b]
$BaMg_2RuH_8$	$[RuH_6]^{4-}, H^-$	2.7	98	>400°	[19]
Mg_2CoH_5	$[CoH_5]^{4-}$	4.5	126	280°	[2]
$Mg_6Co_2H_{11}$	$[CoH_4]^{5-}, [CoH_5]^{4-}, H^-$	4.0	97	370°	[2]
$Ca_4Mg_4Co_3H_{19}$	$[CoH_5]^{4-}, H^-$	4.2	106	>480°	[11]
Mg_2NiH_4	$[NiH_4]^{4-}$	3.6	98	280°	[2]
$CaMgNiH_4$	$[NiH_4]^{4-}$	3.2	87	405°	[2]
$Ba_7Cu_3H_{17}$	$[CuH_4]^{3-}, H^-$	1.5	63	<100°	[13]
K_2ZnH_4	$[ZnH_4]^{2-}$	2.7	57	310°	[14a]
K_3ZnH_5	$[ZnH_4]^{2-}, H^-$	2.7	56	360°	[14a]
Mg_2RuH_4	$[RuH_4]^{4n-}$	2.6	95	>400°	[2]
Mg_3RuH_3	$[RuH_3]^{6-}$	1.7	54	>400°	[2]
$LiSr_2PdH_5$	$[PdH_3]^{3-}, H^-$	1.7	74	>400°	[2]

^a) discovered and/or analysed at the University of Geneva, listed in decreasing order of the hydrogen liganacy of the transition metal

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	complex	electron configuration	electrons per complex
	[ReH ₉] ²⁻ [TcH ₉] ²⁻	(d ⁰)-d ⁵ sp ³ (d ⁰)-d ⁵ sp ³	18 18
	[MnH ₆] ⁵⁻ [ReH ₆] ⁵⁻ [FeH ₆] ⁴⁻ [RuH ₆] ⁴⁻ [OsH ₆] ⁴⁻ [RhH ₆] ³⁻ [IrH ₆] ³⁻ [PtH ₆] ²⁻	(d ⁶)-d ² sp ³ (d ⁶)-d ² sp ³ (d ⁶)-d ² sp ³ (d ⁶)-d ² sp ³ (d ⁶)-d ² sp ³ (d ⁶)-d ² sp ³ (d ⁶)-d ² sp ³ (d ⁶)-d ² sp ³	18 18 18 18 18 18 18 18
	[RuH ₅] _{av} ⁵⁻ [CoH ₅] ⁴⁻ [IrH ₅] _{av} ⁴⁻	(d ⁸)-dsp ³ (d ⁸)-dsp ³ (d ⁸)-dsp ³	18 18 18
	[RhH ₄] ³⁻ [PdH ₄] ²⁻ [PtH ₄] ²⁻	(d ⁸)-dsp ² (d ⁸)-dsp ² (d ⁸)-dsp ²	16 16 16
	[MnH ₄] ²⁻ [NiH ₄] ⁴⁻ [CuH ₄] ³⁻ [ZnH ₄] ²⁻	(d ⁵)-sp ³ (d ¹⁰)-sp ³ (d ¹⁰)-sp ³ (d ¹⁰)-sp ³	13 18 18 18
	[CoH ₄] _{av} ⁵⁻ [RuH ₄] ⁴⁻	(d ⁸)-dsp ³ (d ⁸)-dsp ²	18 16*)
	[RuH ₃] ⁶⁻ [PdH ₃] _{av} ³⁻	? (d ¹⁰)-sp ²	17*) 16
	[PdH ₂] ²⁻	(d ¹⁰)-sp	14

Fig. 1. Ligand geometries, likely electron configurations and electron counts for transition-metal hydrido complexes; av: average due to disorder; *) possible metal-metal bonds (see text)

als by solid-state reactions from the elements and/or binary hydrides (MH or MH₂) at temperatures typically between 300 and 500°, and hydrogen pressures between 1 and 100 bar. Some, however, can only be prepared by solution methods, reaction in a high-temperature anvil pressure cell, mechanical alloying, or the use of a LiH flux to increase the yield (see examples below).

2.2. Structures and Properties

For the structural characterisation of complex transition-metal hydrides, complementary methods such as neutron diffraction on deuterides, high-resolution X-ray (synchrotron) diffraction, NMR and IR spectroscopy, and advanced data analysis methods are essential. The enthalpies of hydride formation are generally determined from *van't Hoff* plots of plateau pressures as measured from pressure-composition isotherms.

The range of compounds known is very large. Those investigated in Geneva are listed in *Table 1* together with hydrogen storage efficiencies and hydrogen desorption temperatures.

The most striking structural features are the transition-metal hydrido complexes [TH_x]ⁿ⁻ ($x = 2-9$, $n = 2-5$) which adopt various ligand geometries and electronic configurations as shown in *Fig 1*. Some structures also contain hydrogen anions H⁻ bonded to non-transition metals only.

Together, these two hydride species lead to a great variety of crystal structures and properties. In the following, they will be discussed by referring [5] to typical representatives of the most common ligand geometries. The various crystal structures are represented in *Fig. 2*.

2.2.1. Tricapped Trigonal Prismatic Complexes

BaReH₉, was prepared by a solution method [6a]; the hexagonal structure contains [ReH₉]²⁻ 18-electron complexes, whose H positions were inferred from IR and NMR data. It has the highest hydrogen-to-metal ratio known (H/M = 4.5), a good hydrogen volume efficiency (134 g/l) and a low dissociation temperature (<100° at 1 bar), but is too heavy (weight efficiency 2.7%) and too expensive for large-scale storage applications. No analogues (except for technetium) are known. [ReH₉]²⁻ complexes also occur in K₂ReH₉ and NaKReH₉ [6b] which desorb hydrogen below 100°.

2.2.2. Octahedral Complexes

Mg₂FeH₆: originally prepared as a green powder by sintering at 500° and 20-

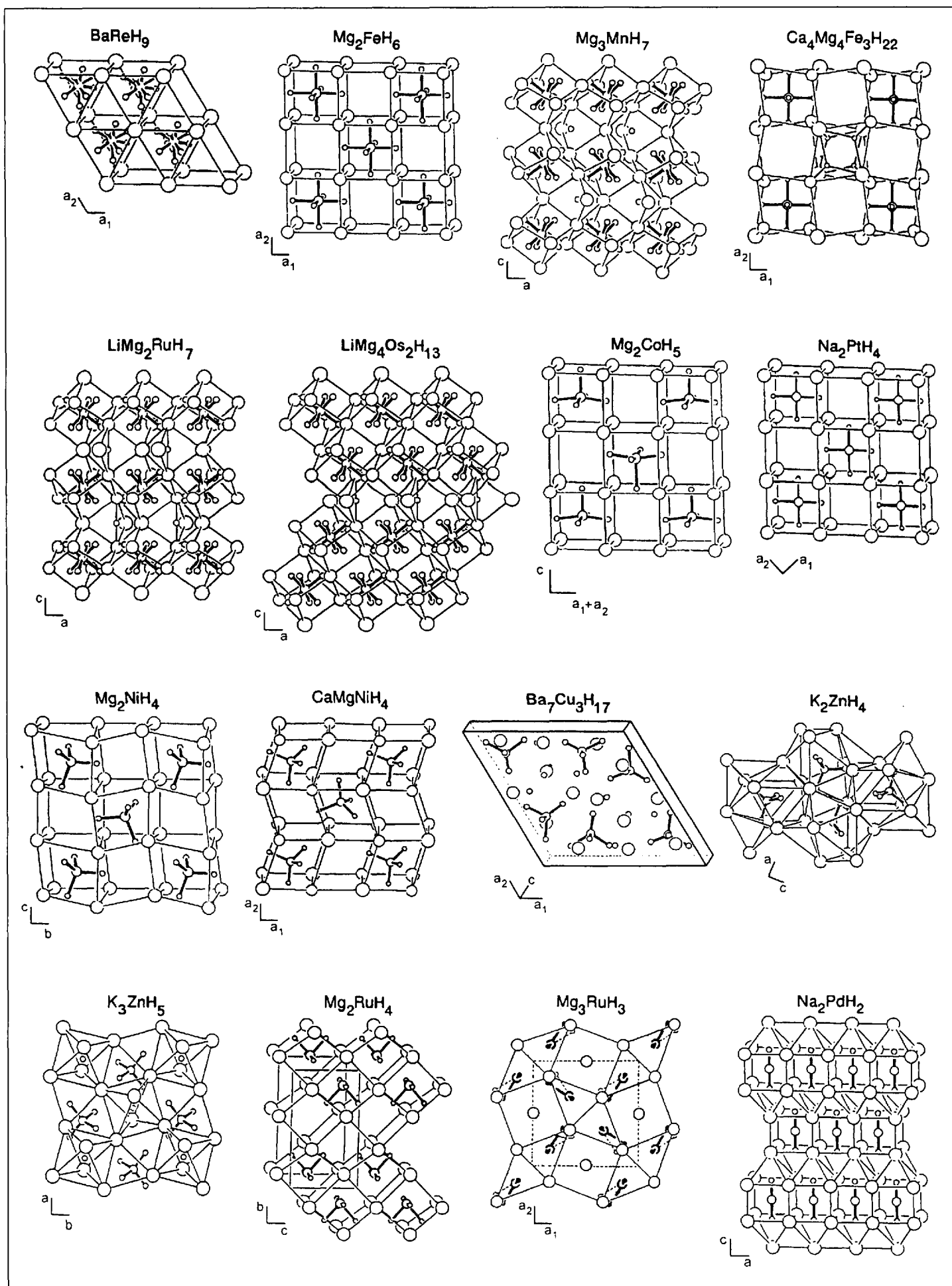


Fig. 2. Crystal structures of solid-state complex transition-metal hydrides. TH_x complexes are drawn by heavy lines, disordered ligands by dashed lines, M-M contacts by single lines, M as large circles, and H^- as small isolated circles.

120 bar hydrogen pressure, it can also be obtained under milder conditions by mechanical alloying. The cubic K_2PtCl_6 -type structure contains octahedral $[FeH_6]^{4-}$ 18-electron complexes which are surrounded by Mg^{2+} in a cubic configuration. It has a very high hydrogen volume storage efficiency (150 g/l), a good weight efficiency (5.4 wt.%) and is cheap to fabricate, but it is too stable for reversible storage applications at room temperature (desorption enthalpy $\Delta H = 98$ kJ/mole H_2 , decomposition temperature at 1 bar is 320°). It is nonmetallic and *Mössbauer* spectra are consistent with low-spin Fe^{II} . Analogues exist for M_2TH_6 ($M = Mg, Ca, Sr, Yb, Eu$; $T = Fe, Ru, Os$) and M_2PtH_6 ($M = Na, K$ [3]); most are moisture-sensitive and some are pyrophoric (Mg_2OsH_6); due to matrix effects, the $Fe-H$ bond distances increase from 1.56 Å to 1.62 Å if Mg is substituted by Ca; $(H-H)_{min} = 2.20$ Å; force fields of Mg_2FeH_6 and its deuteride are known from inelastic neutron scattering [7]; IR stretching frequencies of $T-H$ bonds range from 1450 to 1850 cm^{-1} ; they increase in the sequence $T = Fe, Ru, Os$, and decrease as the ionic size of M^{2+} increases; theoretical band gaps range from 1.3 eV (Sr_2FeH_6) to 4.0 eV (Mg_2OsH_6); most compounds are diamagnetic, except Eu_2RuH_6 (red) which is paramagnetic with $\mu_{eff} = 7.7 \mu_B$ and orders magnetically below $T_C = 49K$; octahedral $[FeH_6]^{4-}$ complexes also occur in quaternary $SrMg_2FeH_8$ [8].

Mg_3MnH_7 : recently prepared as a reddish powder by application of high pressure (20 kbar) in a multi-anvil cell [9]. The hexagonal structure contains octahedral $[Mn^IIH_6]^{5-}$ 18-electron complexes ($Mn-H = 1.63$ Å); an additional hydride anion is coordinated by a Mg^{2+} trigonal bipyramid ($H-Mg = 1.87$ Å (2x), 2.71 Å (3x)); $(H-H)_{min} = 2.29$ Å). The compound has promising hydrogen storage properties: 5.2 wt.%, 118.5 g H_2/l , decomposition at 1 bar starts at 240° . An isostructural rhenium analogue exists.

$Ca_4Mg_4Fe_3H_{22}$: typical example for a quaternary hydride that derives from a ternary hydride (Mg_2FeH_6) by ordered cation substitution. In the cubic structure, every fourth $[FeH_6]^{4-}$ is replaced by four hydrogen anions which are tetrahedrally coordinated by M^{2+} ; $Fe-H = 1.56-1.58$ Å, $M-H = 1.81$ Å (Mg), 2.39 Å (Ca), $(H-H)_{min} = 2.22$ Å; is thermally more stable ($\Delta H = 122$ kJ/mole H_2) than Mg_2FeH_6 ; decomposes in two steps *via* Ca_2FeH_6 ; brownish translucent single crystals can be grown in a LiH flux.

$LiMg_2RuH_7$: typical example for an intergrowth structure obtained by reaction of Mg_2RuH_6 with LiH; the hexagonal

structure [10a] shows Mg_2RuH_6 like slabs made up by single layers of octahedral $[RuH_6]^{4-}$ complexes which are intergrown with LiH sheets; $Ru-H = 1.70$ Å; $(H-H)_{min} = 2.46$ Å; H^- anions have a trigonal bipyramidal coordination by Li^+ and Mg^{2+} ($M-H = 1.85$ Å (2 Mg), 2.71 Å (3 Li)). An isostructural analogue exists for osmium, but not for iron.

$LiMg_4Os_2H_{13}$: hexagonal intergrowth structure as above, except that the Mg_2OsH_6 like slabs are made up by double layers of octahedral $[OsH_6]^{4-}$ complexes [10b]; $Os-H = 1.70$ Å; $(H-H)_{min} = 2.31$ Å); evidence for an isostructural analogue exists for ruthenium, but not for iron.

2.2.3. Square-Pyramidal Complexes

Mg_2CoH_5 : tetragonal structure, similar to cubic Mg_2FeH_6 , except that it contains square-pyramidal $[CoH_5]^{4-}$ 18-electron complexes ($Co-H = 1.52$ Å (basal), 1.59 Å (apical)); $(H-H)_{min} = 2.12$ Å; transforms at 488 K into a disordered cubic high-temperature (HT) modification; presumably nonmetallic; theoretical band gap 1.9 eV, weakly paramagnetic (possibly diamagnetic); $\Delta H = 86$ kJ/mole H_2 ; evidence for isostructural iridium analogues M_2IrH_5 ($M = Mg, Ca, Sr$), but not for rhodium analogue Mg_2RhH_5 ; square-pyramidal hydride complexes presumably also occur in partially disordered $Mg_6Co_2H_{11}$, Mg_3RuH_6 [3] and $M_4Mg_4Co_3H_{19}$ ($M = Ca, Yb$) [11].

2.2.4. Square-Planar Complexes

Na_2PtH_4 : tetragonal structure [3] contains $[Pt^{II}H_4]^{2-}$ 16-electron complexes ($Pt-H = 1.64$ Å) surrounded by Na^+ in a cubic configuration; $(H-H)_{min} = 2.32$ Å; transforms at *ca.* 300° into a disordered cubic HT modification; red-violet, nonmetallic, diamagnetic powder; theoretical band gap 1.2 eV; Pd, Cs and K analogues exist; square-planar complexes also occur in Li_3RhH_4 , K_2PtH_4 , K_3PtH_5 and Ba_2PtH_6 ; those in K_2PtH_4 undergo in-plane rotational motions as shown by NMR data.

2.2.5. Tetrahedral Complexes

Mg_2NiH_4 : monoclinic structure contains tetrahedral $[NiH_4]^{4-}$ 18-electron complexes which are surrounded by Mg^{2+} in a strongly distorted cubic configuration; sp^3 bonded Ni^0 has bond lengths $Ni-H = 1.54-1.57$ Å and bond angles $H-Ni-H = 103-119^\circ$; $(H-H)_{min} = 2.43$ Å; dark-red (fully hydrided) or brownish (partially hydrided) powder; diamagnetic and nonmetallic; can be obtained by hydrogenation of the binary alloy Mg_2Ni , and by mechanical alloying; microtwinning parallel to the *bc*

plane is consistent with a structural transformation at *ca.* 230° into a disordered cubic HT modification; theoretical band gap 1.8 eV; has a good hydrogen storage efficiency: 3.6 wt.%, 98 g/l; thermal stability ($\Delta H = 64$ kJ/mole H_2 , desorption temperature 280° at 1 bar) is sufficiently low for reversible hydrogen storage applications in automobiles; no structural analogues are known.

$CaMgNiH_4$: ordered quaternary derivative of Mg_2NiH_4 ; the cubic structure contains a tetrahedral $[Ni^0H_4]^{4-}$ 18-electron complex which is surrounded by a strongly distorted M^{2+} cube; $Ni-H = 1.60$ Å, $M-H = 2.08$ Å (Mg), 2.45 Å (Ca); $(H-H)_{min} = 2.59$ Å; greenish powder; translucent single crystals of yellow-brownish colour can be obtained in a LiH flux; thermal stability ($\Delta H = 129$ kJ/mole H_2) is twice that of Mg_2NiH_4 ; isostructural Sr and Yb analogues exist [12].

$Ba_7Cu_3H_{17}$: first structurally characterised hydrido Cu complex [13]; the trigonal structure contains tetrahedral $[CuH_4]^{3-}$ 18-electron complexes ($Cu-H = 1.6-1.78$ Å) and three types of tetrahedrally coordinated H^- anions ($Ba-H = 2.50-2.92$ Å); Cu^I is presumably sp^3 hybridized similar to Ni^0 in Mg_2NiH_4 and Zn^{II} in K_2ZnH_4 ; conspicuously short $(H-H)_{min} = 1.94(4)$ Å; prepared by hydrogenation of binary alloy at room temperature; no analogues are known.

K_2ZnH_4 and K_3ZnH_5 : first structurally characterised hydrido Zn complexes [14a]; the orthorhombic and tetragonal structures, respectively, contain tetrahedral $[Zn^{II}H_4]^{2-}$ complexes ($Zn-H = 1.63-1.67$ Å); K_3ZnH_5 also contains hydrogen anions ($H-K = 2.77-2.79$ Å); $(H-H)_{min} = 2.66$ Å; prepared by solid-state reaction and solution methods; decompose *via* binary hydrides; $Zn-H$ bond lengths in Rb and Cs analogues increase to 1.67–1.70 Å [14b] due to matrix effects; magnetic Mn analogues M_3MnH_5 ($M = K, Rb, Cs$) of pink colour have been recently synthesised at *ca.* 500° under 3 kbar hydrogen gas pressure [15].

2.2.6. Saddle-Like Complexes

Mg_2RuH_4 : orthorhombic structure contains a saddle-like $[Ru^0H_4]^{4-}$ 16-electron complex which derives from octahedral $[Ru^{II}H_6]^{4-}$ by removal of two *cis* H ligands ($Ru-H = 1.67-1.68$ Å; $H-Ru-H = 84.2^\circ, 93.6^\circ$ (*cis*), 170.3° (*trans*)); $(H-H)_{min} = 2.23$ Å; complexes are surrounded by Mg^{2+} in a cubic configuration; possible Ru-Ru interactions across neighbouring cube faces ($Ru-Ru = 3.24$ Å) could lead to polyanionic $[Ru_nH_{4n}]^{4n-}$ zig-zag chains running along *c*; reddish-brown to dark-red

colour; magnetic measurements consistent with d^8 low-spin configuration; no Fe analogue is known; saddle-like complexes presumably also occur in partially disordered $Mg_6Co_2H_{11}$ ($[CoH_4]^{5-}$).

2.2.7. T-Shaped Complexes

Mg₃RuH₃: tetragonal structure contains orientationally disordered T-shaped RuH_3 units ($Ru-H = 1.71 \text{ \AA}$, $(H-H)_{\min} = 2.52 \text{ \AA}$) which are possibly joined to dimers by a $Ru-Ru$ bond (3.31 \AA); T-shaped $[PdH_3]^{3-}$ units presumably occur in partially disordered $LiSr_2PdH_5$; triangular $[PdH_3]^{3-}$ units occur in ordered $NaBaPdH_3$ [4].

2.2.8. Linear Complexes

Na₂PdH₂: tetragonal structure [3] contains linear $[Pd^0H_2]^{2-}$ 14-electron complexes ($Pd-H = 1.68 \text{ \AA}$) surrounded by Na^+ in a bicapped cubic configuration; melts at 408° without decomposing; metallic conductivity measured on single crystals; electronic band-structure calculations predict filled d bands and metallic properties in two dimensions (ab plane); linear complexes also occur in K_3PdH_3 .

3. Systematic Trends and Predictive Concepts

3.1. Structural Features

3.1.1. Hydrogen, a Very Flexible Ligand

The large inventory of complex transition-metal hydrides reflects the special bonding character of hydrogen which can occur in the same structure as a covalently bonded ligand and as an anion. Its small atomic size and high-field ligand character favours 18-electron compounds (about 70 representatives with group 7–10 elements including Cu and Zn). Compounds with 16 electrons (over a dozen representatives with Rh, Pd and Pt), or 14 electrons (half a dozen representatives with Pd and Pt) are less numerous. On the other hand, the relative softness of hydrogen as a ligand and the relative stability of hydrogen as an anion favour structural diversity. Illustrative examples are the quaternary hydrides $Ca_4Mg_4Fe_3H_{22}$ and $Ca_4Mg_4Co_3H_{19}$ which derive from ternary Mg_2FeH_6 and Mg_2CoH_5 , respectively, by the substitution of one fourth of the tetravalent transition-metal complexes by four H^- anions each. Other examples are Mg_3MnH_7 , $Mg_6Co_2H_{11}$ and Mg_3RuH_6 which have similar metal-atom substructures and yet are capable of accommodating rather different complex geometries and hydrogen anions.

Table 2. Homoleptic Transition-Metal Hydrogen Complexes

Mn	Fe	Co	Ni	Cu	Zn
$[MnH_4]^{2-}$	$[FeH_6]^{4+}$	$[CoH_4]_{av}^{5-}$	$[NiH_4]^{4+}$	$[CuH_4]^{3-}$	$[ZnH_4]^{2-}$
$[MnH_6]^{5-}$		$[CoH_5]^{4+}$			
Tc	Ru	Rh	Pd	Ag	Cd
$[TcH_9]^{2-}$	$[RuH_3]^{6-}$	$[RhH_4]^{3-}$	$[PdH_2]^{2-}$		
	$[RuH_4]_{av}^{4n-}$	$[RhH_6]^{3-}$	$[PdH_3]^{3-}$		
	$[RuH_5]_{av}^{5-}$		$[PdH_4]^{2-}$		
	$[RuH_6]^{4+}$				
Re	Os	Ir	Pt	Au	Hg
$[ReH_6]^{5-}$	$[OsH_6]^{4+}$	$[IrH_5]_{av}^{4-}$	$[PtH_4]^{2-}$		
$[ReH_9]^{2-}$		$[IrH_6]^{3-}$	$[PtH_6]^{2-}$		
			$[Pt_2H_9]^{5-}$		

av: average due to disorder

3.1.2. Hydrido Complexes

Their occurrence across the transition-metals series is shown in Table 2. The trend goes from high-coordinate at the left (group 7) to low-coordinate at the right (group 10). The complexes are generally mononuclear and have terminal hydrogen ligands. Of particular interest are the members of the 3d series, including Cu and Zn. They all form homoleptic hydrido complexes. Some adopt only one ligand geometry such as Ni, Cu and Zn (tetrahedral), while others adopt two geometries such as Mn (octahedral or tetrahedral) or Co (saddle-like or square-pyramidal). The most prolific transition metal is Ru which adopts four geometries (saddle-like, T-shaped, square-pyramidal, octahedral), in contrast to its Fe congener which adopts only one (octahedral). Each hydride structure contains only one type of hydrido complex. Notable exceptions are K_2ReH_9 (two crystallographically different $[ReH_9]^{2-}$) and $Mg_6Co_2H_{11}$ ($[CoH_4]^{5-}$ and $[CoH_5]^{4+}$). The only dinuclear complex known is $[Pt_2H_9]^{5-}$ which has a bridging hydrogen and occurs in $Na_5Pt_2H_9$ [16]. Hydrides containing heteronuclear complexes, or complexes formed by different transition metals have not yet been reported.

The hydrogen ligand geometries are consistent with those expected for transition metals in coordination compounds, *i.e.*, they are octahedral such as in $Mo(CO)_6$ (d^6 , 18 electrons), square-planar such as in $Ni(CN)_4^{2-}$ (d^8 , 16 electrons) and tetrahedral such as in $Ni(CO)_4$ (d^{10} , 18 elec-

trons). The square-pyramidal and saddle-like geometries are similar to those in $Co(CN)_5^{3-}$ (d^7 , 17 electrons) and $Ru(CO)_4$ ($\equiv Ru_3(CO)_{12}$; d^8 , 18 electrons (see below), respectively. Linear coordinations are also not uncommon for d^{10} systems. A trigonal bipyramidal hydrogen configuration similar to the ligand geometry in $Fe(CO)_5$ has not yet been reported. Some geometries represent only averages such as $[CoH_4]_{av}^{5-}$, $[RuH_5]_{av}^{5-}$, $[PdH_3]_{av}^{3-}$ and $[IrH_3]_{av}^{6-}$ because of disorder. The mobility of the hydrogen ligands (or complexes) at room temperature is generally high. Well-characterised order-disorder transitions at or near room temperature occur in Mg_2CoH_5 , Mg_2NiH_4 , K_3PdH_3 , Na_2PtH_4 , M_3PtH_5 , ($M = Rb, Cs$) and M_2PtH_4 , ($M = K, Rb, Cs$).

3.1.3. Hydrogen Anions

They occur in about half of the structures known and appear to be preferentially associated with 18-electron systems; the H^- anions are coordinated by M^+ and/or M^{2+} cations in mostly tetrahedral ($SrMg_2FeH_8$, $BaMg_2RuH_8$, $Ca_4Mg_4Fe_3H_{22}$) and linear (or trigonal bipyramidal) configurations ($LiMg_2RuH_7$, Mg_3MnH_7). Unlike the hydrogens in the complex, they are neither mobile nor disordered.

3.1.4. Formal Oxidation Numbers

The formal charges and electron counts can be rationalised in terms of limiting ionic formulas such as $Mg_3MnH_7 = 3Mg^{2+} \cdot [MnH_6]^{5-} \cdot H^-$ (18 electrons),

$\text{Na}_2\text{PtH}_4 = 2\text{Na}^+[\text{PtH}_4]^{2-}$ (16 electrons) and $\text{Na}_2\text{PdH}_2 = 2\text{Na}^+[\text{PdH}_2]^{2-}$ (14 electrons). The formal oxidation numbers of the transition elements range from *zero* (Ru, Ni, Pd) to *I* (Mn, Re, Co, Ir, Rh, Cu), *II* (Fe, Ru, Os, Pd, Pt, Zn), *III* (Ir, Rh), *IV* (Pt) and *VII* (Re). The situation in Mg_2RuH_4 is of particular interest because its structure and electron count (formally 16 electrons/Ru) suggest Ru–Ru two-electron bonds (two per Ru) which are linking the $[\text{RuH}_4]^{4-}$ units to polymeric $(\text{Ru}_n\text{H}_{4n})^{4n-}$ zig-zag chains. Thus, each Ru could 'see' 18 electrons, although the metal-metal distances (Ru–Ru = 3.24 Å) are considerably longer than those in the metal-metal bound trimer $\text{Ru}_3(\text{CO})_{12}$ (Ru–Ru *ca.* 2.85 Å). Another intriguing case is Mg_3RuH_3 (formally 17 electrons/Ru) which can be formulated as an 18-electron compound by postulating a Ru–Ru two-electron bond connecting two $[\text{RuH}_3]^{6-}$ monomers to a $[\text{Ru}_2\text{H}_6]^{12-}$ dimer. The possibility of Ru–Ru bond formation in these compounds has been investigated theoretically [17].

3.1.5. Metal-Hydrogen Bonds

The T–H bond distances are in the range 1.50–1.60 Å for 3d metals, and 1.70–1.80 Å for 4d and 5d metals except for low-coordinate Pd (1.60–1.70 Å) and Pt (1.58–1.67 Å). Due to matrix effects the bond lengths scale with the size of the M cations. The M–H bond distances of the complex hydrogen are generally longer than those in the corresponding binary metal hydrides. However, those of the anionic hydrogen – which is relatively low-coordinate – are significantly shortened (Mg–H = 1.81–1.87 Å, Ba–H = 2.50 Å, K–H = 2.77 Å) compared to the relatively high coordinate hydrogen in the corresponding binary metal hydrides MgH_2 (1.95 Å), BaH_2 (2.57 Å) and KH (2.85 Å).

3.1.6. Hydrogen-Hydrogen Contacts

The H–H contacts usually exceed 2.1 Å, and thus indicate nonbonding (or repulsive) interactions. Contacts at less than 2.0 Å occur in K_2ReH_9 and $\text{Ba}_7\text{Cu}_3\text{H}_{17}$. There is no evidence for hydrogen pairing, unlike for molecular transition-metal hydride complexes in which di-hydrogen groups are known to occur [18].

3.2. Properties

3.2.1. Electric Conductivity, Colour, Magnetism, Vibrational Spectroscopy

The quality and completeness of the published data generally depend on the availability of suitable single crystals; most complex transition-metal hydrides are

polycrystalline and either experimentally found or theoretically predicted to be non-metallic; many are coloured; only few are metallic such as Li_2PdH_2 and Na_2PdH_2 ; many are diamagnetic, as expected from closed-shell configurations associated with low-spin d^6 (octahedral), d^8 (square-planar) and d^{10} (tetrahedral, linear) configurations; the compounds containing magnetic ions such as Eu^{2+} and Mn^{2+} show temperature-dependent paramagnetism and order magnetically at low temperature. The known vibrational spectra (IR, inelastic neutron scattering) correlate with bonding properties, such as in the K_2PtCl_6 -type series, for which the T–H stretching frequencies increase in the sequence T = Fe, Ru, Os, and decrease as the M–H bond lengths increase. However, the picture concerning the electric, magnetic and spectroscopic properties is far from being complete, and more data are needed.

3.2.2. Hydrogen Storage Efficiencies

The hydrogen-to-metal ratios reach values of up to H/M = 4.5 (BaReH_9) and thus surpass the hydrogen-to-carbon ratios of hydrocarbons (methane: H/C = 4); the hydrogen volume efficiencies reach 150 g/l (Mg_2FeH_6) and thus exceed that of liquid hydrogen (71 g/l) by a factor of up to two. The weight efficiencies exceed 5% (Mg_2FeH_6 , Mg_3MnH_7).

3.2.3. Thermal Stability

The hydrides decompose in one or several steps with upper plateau temperatures at 1 bar hydrogen pressure in the range of *ca.* 100° (NaKReH_9) to 400° (CaMgNiH_4). The desorption enthalpies known cover the range $\Delta H = 64$ –130 kJ/mole H_2 ; they are intermediate between those of typically metallic hydrides such as LaNi_5H_6 ($\Delta H = 31$ kJ/mole H_2) and saline hydrides such as LiH ($\Delta H = 181$ kJ/mole H_2). Due to the scarcity of data, no satisfactory model exists which is capable of rationalising these enthalpies. Interactions between hydrogen and alkaline and/or alkaline-earth elements appear to play a role, as can be seen from the two substitutional pairs Mg_2NiH_4 ($\Delta H = 64$ kJ/mole H_2) – CaMgNiH_4 ($\Delta H = 129$ kJ/mole H_2) and Mg_2FeH_6 ($\Delta H = 98$ kJ/mole H_2) – $\text{Ca}_4\text{Mg}_4\text{Fe}_3\text{H}_{22}$ ($\Delta H = 122$ kJ/mole H_2), in which the stability increases strongly as one goes from the Mg-based ternary to the Ca-containing quaternary compound. This trend correlates with the thermal stability of binary CaH_2 ($\Delta H = 184$ kJ/mole H_2) which is much higher than that of MgH_2 ($\Delta H = 74$ kJ/mole H_2). Clearly, more data are necessary to put this type of correlation on a more quantitative basis.

3.3. Criteria for Hydride Formation

3.3.1. Magic Electron Numbers

In contrast to metallic transition-metal hydrides, the composition of complex transition-metal hydrides can be rationalised in terms of 'magic' electron counts. The Mg_2FeH_6 – Mg_2CoH_5 – Mg_2NiH_4 series provides an illustrative example. Its hydrogen content decreases as the number of available d electrons increases, in accordance with the 18-electron rule. The usefulness of this approach is also apparent for 16- and 14-electron systems, and for hydride structures that contain both complex and anionic hydrogen, such as $\text{Ca}_4\text{Mg}_4\text{Fe}_3\text{H}_{22}$ and K_3ZnH_5 . Their compositions clearly depend on the electron count of the complex and the valence of the metal cations. Thus the concept of 'magic' electron numbers has considerable predictive value.

3.3.2. Structural Intergrowth

Illustrative examples are the quaternary hydrides $\text{LiMg}_2\text{OsH}_7$ ($\text{Li}^+\text{H}^- \cdot 2\text{Mg}^{2+} \cdot [\text{OsH}_6]^{4-}$) and $\text{LiMg}_4\text{Os}_2\text{H}_{13}$ ($\text{Li}^+\text{H}^- \cdot 4\text{Mg}^{2+} \cdot 2[\text{OsH}_6]^{4-}$) which derive from ternary Mg_2OsH_6 by intergrowth with LiH. These can be considered as the first members ($n = 1, 2$) of a structural series having the general composition $\text{LiMg}_{2n}\text{Os}_n\text{H}_{6n+1}$. The existence of members with $n > 2$ is likely but not yet demonstrated. The intergrowth concept also applies to trigonal $\text{SrMg}_2\text{FeH}_8$ (Mg_2FeH_6 intergrown with SrH_2) and tetragonal $\text{BaMg}_2\text{RuH}_8$ (Mg_2RuH_6 intergrown with BaH_2) [19] although their M^{2+} substructures become somewhat distorted.

3.3.3. Substitutional Derivatives

Quaternary metal hydride structures which can be considered as ordered derivatives of ternary hydride structures are $\text{Ca}_4\text{Mg}_4\text{Fe}_3\text{H}_{22}$, $\text{Ca}_4\text{Mg}_4\text{Co}_3\text{H}_{19}$ and CaMgNiH_4 . The concept of atomic substitution is useful but obviously limited by matrix effects. The absence of Fe analogues for the various Ru and Os members of the above LiH intergrowth series, *e.g.*, could be due to a size mismatch between the relatively small $[\text{FeH}_6]^{4-}$ complexes and the Li cations. Similar effects could also be responsible for the apparent absence of ternary hydrides such as 'MgMnH₉', a possible derivative of isoelectronic BaReH_9 .

3.3.4. Competing Phases

The thermodynamics of the phase diagram are also important; this can be seen from the Mg–Rh–H system in which the competing phases Mg_2RhH_x ($x \sim 1$) and Mg_2Rh presumably prevent the formation

of the expected hydride phase 'Mg₂RhH₅'. The absence of complex hydrides with early transition metals, such as Sc, Ti, V *etc.*, could have similar reasons. In contrast to late transition metals, the latter form stable binary hydrides and intermetallic compounds with M elements, and this could prevent the formation of complex hydrides.

3.3.5. Influence of Pressure

A decisive parameter for hydride formation is pressure. The synthesis of hydrides based on light transition elements usually requires higher hydrogen pressures than that based on heavier congeners. Examples are the Pd compounds M₂PdH₄ and M₃PdH₅ which form at 20 and 70 bar, respectively, in contrast to their Pt congeners, which form already at 1 bar. For a given transition metal, an increase of hydrogen pressure usually allows to stabilise higher formal oxidation states. Examples are found for palladium in M₃Pd⁰H₃ and M₂Pd^{II}H₄ which form at 1 bar and 20 bar, respectively, for platinum in K₂Pt^{II}H₄ and K₂Pt^{IV}H₆ which form at 1 bar and 1800 bar, respectively, and for ruthenium in Mg₂Ru⁰H₄ and Mg₂Ru^{II}H₆ which form at 20 bar and 90 bar, respectively [3]. However, the inverse situation appears to prevail for manganese-based Mg₃Mn^IH₇ which forms under a mechanical pressure of 20 kbar, while K₃Mn^{II}H₅ forms under a gas pressure of 3 kbar only. It is reasonable to expect that high-pressure techniques, together with other synthetic routes such as solution methods and mechanical alloying, will give access to further members of this class of compounds.

4. Summary

Complex transition-metal hydrides constitute a fascinating class of solid-state compounds. They have a rich crystal chemistry which combines features of coordination compounds and saline hydrides. Their structures are built up by homoleptic transition-metal complexes which have up to nine ligands, by hydrogen anions and by non-transition-metal cations. Hydrogen acts as a strong and flexible ligand which is capable of oxidising heavy transition elements to oxidation numbers of up to IV (Pt) and even VII (Re). Spectroscopic, magnetic and thermodynamic properties have been reported but need to be completed. Many compounds have excellent hydrogen storage efficiencies, but are either thermally too stable or too expensive for applications at room temperature.

The main object of future work is to find advanced materials that combine high storage efficiency, low thermal stability and low fabrication costs, and to understand better the factors which influence thermodynamic properties. Some useful concepts for search exist, such as 'magic' electron counts, structural intergrowth and ordered substitution, and they need to be augmented by the use of new synthetic methods. Preliminary thermodynamic data provide a first step towards a better understanding of their thermal stability.

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