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Structure and bonding in homoleptic transition metal hydride anions

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Abstract

This paper surveys aspects of the structure and bonding in homoleptic transition metal hydride anions. Most such hydrometalate anions are found in solid state ternary and quaternary transition metal hydrides also containing one or two electropositive metals although soluble MH_9^{2-} (M = Tc, Re) and FeH_6^{4-} derivatives are known. The principles of structure and bonding in such hydrometalates are seen to be similar to those in related transition metal complexes of other ligands. Thus the favored 18-electron configuration of the next rare gas dominates for the hydrometalates of manganese (in MnH_6^{5-}) through copper (in CuH_4^{3-}) although square planar and trigonal 16-electron complexes (e.g. PdH_3^{3-}, PdH_4^{2-}, and PtH_4^{2-}) and linear 14-electron complexes (PdH_2^{2-}) are also known. The stability of a half filled d shell for the d^5 Mn(II) is illustrated by the occurrence of the high-spin tetrahedral MnH_4^{2-} ion in K_3MnH_5. The metal atoms in the RuH_4^{4-} units of Mg_2RuH_4 and the RuH_3^{6-} units of Mg_3RuH_3 can attain the 18-electron rare gas configuration through metal-metal bonding to form the polymer $[RuH_4^{4-}]_\infty$ and the dimer $[RuH_3^{6-}]_2$, respectively. The RhH^{2-} anion in MgRhH forms a cyclic tetramer related but not identical to the cyclic tetramers formed by certain isoelectronic Cu(I) alkyls.

Keywords: Structure; Bonding; Homoleptic transition; Metal hydride anions

1. Introduction

An important feature of transition metal coordination chemistry is the existence of a variety of stable metal complexes with strong field ligands exhibiting chemistry very different from that of the aqueous solution chemistry of the corresponding uncomplexed metals. Of particular interest are homoleptic transition metal complexes, in which all ligands are the same. Such complexes include the diverse varieties of homoleptic metal carbonyls [1], metal isocyanide complexes [2], and metal cyanide complexes [3], in which the ligands have low-lying π*-orbitals which can stabilize low oxidation states by $d\pi \rightarrow p\pi^*$ backbonding. The favored metal coordination number in such complexes is governed by the so-called 'effective atomic number rule', which confers unusually high stability on metal complexes in which the central metal has the electronic configuration of the next rare gas, namely 18 valence electrons, as indicated by the stable homoleptic metal carbonyls $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ of the first transition series.

Another strong field ligand of interest in transition metal chemistry is the hydride ligand. Heteroleptic transition metal hydride complexes containing one or two hydride ligands as well as other types of ligands around a transition metal center, typically with the 18-electron rare gas configuration, have long been known as exemplified by $HCo(CO)_4$, $(\eta^5\text{-}C_5H_5)_2ReH$, $Rh(CN)_5H^{3-}$, etc. However, the development of the chemistry of homoleptic transition metal hydride complexes (i.e. metal hydride complexes with exclusively hydride ligands) has been relatively slow and even now the only soluble homoleptic transition metal hydride complexes are the hydrometalate anions MH_9^{2-} (M = Tc and Re) and FeH_6^{4-}. This contrasts with main group element chemistry where homoleptic hydrometalates have been known for some time and certain derivatives, notably $LiAlH_4$, are important articles of commerce and have numerous applications, e.g. as reducing agents in organic synthesis [4]. Most known homoleptic transition metal hydrometalates are only known in ternary and more complicated solid state structures, which have been studied most extensively in the laboratories of Yvon in Geneva, Switzerland [5–7], and Bronger in Aachen, Germany [8–10]. The availability of neutron diffraction methods has been essential to understanding the structures of homoleptic transition metal hydrometalates [11].

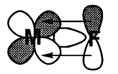
This article surveys the current status of the chemistry of homoleptic transition metal hydrometalates with particular focus on their structure and bonding. For the purpose of this article the transition metals are considered to include the coinage metals (Cu, Ag, Au) but not Zn, Cd, and Hg since the latter three metals do not exhibit well-characterized oxidation states with less than a filled d^{10} shell.

2. Background

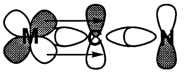
2.1. The hydride ion as a ligand in homoleptic transition metal hydrometalates

It is instructive to compare the properties of the hydride ligand (H^-) with those of two seemingly related uninegative ligands, namely the cyanide and fluoride ligands (Fig. 1). The hydride ligand has only a single s-orbital available for chemical bonding and thus can only participate in metal-ligand σ-bonding with no possibilities for either forward or backwards π-bonding. However the fluoride

Hydride
No π-bonding



Fluoride
Forward pπ→dπ bonding



Cyanide
Backward dπ→pπ* bonding

Fig. 1. A comparison of the bonding of hydride, fluoride, and cyanide ligands to transition metals showing the lack of π-bonding in the M–H bond, the forward π-bonding in the F→M bond, and the backward π-bonding ('backbonding') in the M→CN bond.

ligand has electron pairs and available p-orbitals for forward pπ → dπ* bonding to empty d-orbitals of the central metal atom thereby stabilizing high metal oxidation states as well as more normal oxidation states. Conversely the cyanide ligand has empty π*-orbitals in its C≡N triple bond which can withdraw electron density from filled d-orbitals of the central metal atom through dπ → pπ* back-bonding thereby stabilizing low metal oxidation states as well as more normal oxidation states. Thus the consequences of π-bonding are seen to include both the destabilization of low formal oxidation states by the π-donor fluoride ligand and the destabilization of high oxidation states by the π-acceptor cyanide ligand. The hydride ion, which has no π-bonding ability to destabilize low or high metal formal oxidation states, forms complexes with the central transition metal in a wide range of formal oxidation states ranging from $+7$ in ReH_9^{2-} down to -3 in the IrH_3^{6-} ion found [12] in the solid state material Mg_4IrH_5, both of which have the favored 18-electron rare gas electronic configuration.

The synthesis of homoleptic transition metal hydrometalates is complicated by the fact that the alkali metal hydrides, MH (M = Li, Na, K, Rb, Cs) are insoluble in solvents with which they do not react in contrast to corresponding alkali metal cyanides and fluorides. For this reason direct solution methods for the synthesis of homoleptic transition metal hydrometalates are rarely available and the few known compounds synthesized by solution methods have arisen from reactions so unusual that the products now known to be homoleptic hydrometalates (e.g. ReH_9^{2-} and FeH_6^{4-}) were correctly identified only a few decades after their original synthesis. For this reason most of the homoleptic transition metal hydrometalates occur as anionic units in the structures of ternary solid state materials containing hydrogen, the transition metal, and a highly electropositive metal such as an alkali or alkaline earth metal. Complete ionization of the electropositive metal to its normal cation (M^+ in the case of the alkali metals or M^{2+} in the case of the alkaline earth metals) leaves the homoleptic hydrometalate anion, typically as a discrete monomeric species. For example, the solid state compound Mg_2FeH_6 can be interpreted in this way to consist of $2Mg^{2+} + FeH_6^{4-}$.

These solid state ternary hydrides are prepared by high temperature reactions such as direct combination of the elements in the product or solid state reactions of an alkali or alkaline earth metal hydride with the transition metal and hydrogen at elevated temperatures [13]. Products with higher formal metal oxidation states are favored at higher temperatures and hydrogen pressures as well as with the heavier alkali metals rather than sodium or lithium as counterions. Most of these solid state ternary hydrides are very air-sensitive materials even when they have favored 18-electron configurations and normal transition metal formal oxidation states.

The first soluble homoleptic hydrometalate to be unambiguously characterized was the enneahydrorhenate(VII) ion, ReH_9^{2-} but the route to the discovery of this species was rather tortuous. Rhenium was the last of the non-radioactive transition metals to be discovered [14,15]. In an attempt to prepare a lower oxidation state of rhenium than the $+7$ group oxidation state (e.g. ReO_4^-), a cold dilute solution of ReO_4^- in sulfuric acid was passed through a column of amalgamated zinc (Jones reductor). The resulting colorless air-sensitive solution was analyzed by titration with $KMnO_4$. The results of such titrations were interpreted to imply the presence of −1 rhenium as rhenide, Re^-, analogous to halide since in an obsolete version of the Periodic Table in use at that time rhenium was placed in the same group as the halogens [16]. Preparation of a solid 'rhenide' required different reduction conditions, namely potassium metal in wet ethylenediamine, in order to provide a suitable counterion [17]. Eventually 'rhenides', which were interpreted to contain the square planar $Re(H_2O)_4^-$ anion, were isolated with Li, K, and Ba counterions [18]; the square planar coordination of Re(−I) was postulated by Pauling [19] since Re(−I) is a d^8 transition metal ion isoelectronic with Pt(II) well known to form square planar complexes. Shortly thereafter it was realized that these 'rhenides' are really homoleptic hydrorhenates [20] but the correct identification of these species as ReH_9^{2-} required a structural study by neutron diffraction[21]. The unambiguous identification of ReH_9^{2-} was significant in representing not only the first example of a structurally characterized homoleptic transition metal hydrometalate but also the first example of a nine-coordinate transition metal complex containing exclusively monodentate ligands.

The other known soluble homoleptic transition metal hydrometalate is FeH_6^{4-}, which was also unambiguously characterized only several decades after its initial preparation. In 1923, Schlenk and Weichselfelder [22] found that treatment of anhydrous first row transition metal chlorides with phenylmagnesium bromide in diethyl ether in the presence of H_2 was found to result in the absorption of significant amounts of H_2. These observations were interpreted to indicate the formation of transition metal hydrides, which, however, could not be isolated in the pure state. The reaction of this type using $FeCl_3$ proceeded much more readily than corresponding reactions with the divalent metal chlorides MCl_2 (M = Fe, Co, Ni) because of the much greater solubility of $FeCl_3$ in diethyl ether relative to the divalent metal halides. Analyses of the resulting reaction mixture, from which no pure compound could be isolated, suggested the formula FeH_6 [23]. After some controversy over the nature and composition of this substance [24,25], Gibbins [26] used a complicated procedure to isolate from this mixture a yellow air-sensitive product of composition $FeH_6Mg_4X_4(C_4H_8O)_8$ (X = Cl + Br; C_4H_8O = tetrahydrofuran). The presence of the octahedral FeH_6^{4-} anion in this yellow species was subsequently unambiguously shown by X-ray and neutron diffraction studies [27]. Later work by Linn and Gibbins [28] showed that the solubility of this FeH_6^{4-} derivative could be increased by conversion to alkoxide derivatives of the type $[ROMg(THF)_n]_4[FeH_6]\cdot 4LiX$ by metathesis with a suitable lithium alkoxide. The electronic spectrum of this more soluble FeH_6^{4-} derivative indicated that the ligand field strength of H^- is relatively high (e.g. higher than arsines and chelating amines) but not as high as cyanide or fulminate [29].

2.2. The transition metal valence orbitals in homoleptic hydrometalates

The metal valence orbital manifolds in homoleptic transition metal hydrometalates necessarily include the single s-orbital and all five d-orbitals but may not include the p-orbitals if the energies of the relevant *n*p-orbitals are of significantly higher energy than the *n*s and (*n* − 1)d orbitals. The nine-orbital sp^3d^5 manifold is the typical spherical [30] valence orbital manifold involved in transition metal coordination chemistry [31–34] and is sufficient for understanding the chemical bonding in many transition metal hydrides, particularly those with the favored 18-electron configuration of the next rare gas. However, the six-orbital sd^5 manifold without any p-orbitals may be relevant to understanding some transition metal hydrides, particularly those of the early transition metals. Non-spherical valence orbital manifolds, using only one or two of the three p-orbitals, are also clearly involved in the chemical bonding of some hydrometalates of the later transition metals such as PdH_4^{2-} and PdH_2^{2-}.

The following bonding concepts have been proposed by Landis and co-workers [35–37] for early transition metal hydrides: (a) only s- and d-orbitals are used to form hybrid bond orbitals; (b) the hybrid orbitals have maximal s character (or sd^{n-1} hybridization when making *n* bonds); (c) lone pairs are placed in pure d-orbitals; (d) three-center four-electron (3c-4e) bonds are used when the central metal atom has more than 12 valence electrons.

Furthermore, the s-orbital and all five d-orbitals are gerade orbitals so that an inversion center is not possible for coordination polyhedra using an sd^5 manifold with only two-center two-electron (2c-2e) bonds. The inversion centers present in idealized octahedral and square planar complexes forbid these polyhedra for transition metals using only the six-orbital sd^5 manifold without any p-orbitals and only 2c-2e metal-ligand bonding [30]. This can account for the non-octahedral structures observed for certain six-coordinate early transition metal alkyls such as $W(CH_3)_6$ [38] and $Zr(CH_3)_6^{2-}$ [39]. Similar conclusions arise from the orbitally ranked symmetry analysis method recently presented by Bayse and Hall [40].

Some non-spherical valence orbital manifolds used by the late transition and early post-transition metals can also arise from the shifting of one or two of the outer p-orbitals to such high energies that they no longer participate in the chemical bonding and the accessible spd valence orbital manifold is no longer spherical [41]. If one p-orbital is so shifted to become antibonding, then the accessible spd orbital manifold contains only eight orbitals (sp^2d^3) and has the geometry of a torus or doughnut (Fig. 2(a)). This toroidal sp^2d^5 manifold can bond only in the two-dimensions of the ring of the torus. Filling this sp^2d^5 manifold of eight orbitals with electrons leads to the 16-electron configuration found in square planar complexes of the d^8 transition metals such as Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), and Au(III). Examples of homoleptic hydrometalates with this type of square planar coordination are $Rh^{I}H_4^{3-}$ and $M^{II}H_4^{2-}$ (M = Pd, Pt). The toroidal sp^2d^5 manifold can also lead to trigonal planar and pentagonal planar coordination for three- and five-coordinate complexes, respectively (Fig. 2(b)). An example of a three-coordinate homoleptic hydrometalate with trigonal planar coordination is $Pd^0H_3^{3-}$.

In some structures containing the late transition and post-transition metals two of the outer p-orbitals are raised to antibonding energy levels. This leaves only one p-orbital in the accessible spd-orbital manifold, which now contains seven orbitals (spd^5) and has cylindrical geometry extending in one axial dimension much further than in the remaining two dimensions (Fig. 2(a)). Filling this seven-orbital spd^5

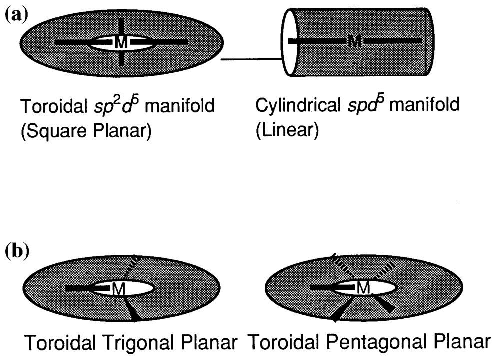


Fig. 2. (a) The toroidal sp^2d^5 and cylindrical spd^5 manifolds showing square planar and linear coordination, respectively. (b) Trigonal and pentagonal planar coordination for the toroidal sp^2d^5 manifold.

manifold with electrons leads to the 14-electron configuration found in two-coordinate linear complexes of d^{10} metals such as Pd(0), Pt(0), Cu(I), Ag(I), and Au(I). An example of a homoleptic hydrometalate with such coordination is $Pd^0H_2^{2-}$.

The p-orbitals, which are raised to antibonding levels as noted above, can participate in $d\sigma \rightarrow p\sigma^*$ or $d\pi \rightarrow p\pi^*$ bonding in complexes of metals with toroidal sp^2d^5, cylindrical spd^5, and spherical sd^5 manifolds depending on the symmetry of the overlap. Such bonding was suggested by Dedieu and Hoffmann [42] in 1978 for Pt(0)–Pt(0) dimers on the basis of extended Hückel calculations and is discussed in detail in a recent review by Pyykkö [43].

Known homoleptic transition metal hydrides [5,8,9] with more than 12 metal valence electrons (including lone pairs) like the octahedral MH_6^{4-} ($M = Fe, Ru, Os$) or square planar $M'H_4^{2-}$ ($M' = Pd$ and Pt) may be formulated as 18 or 16 electron complexes, respectively, with p-orbital participation in the spherical sp^3d^5 or toroidal sp^2d^5 valence orbital manifold discussed below. However, alternative interpretations of these complexes without p-orbital participation but with 3c-4e bonds can be considered analogous to the 3c-4e bonding in hypervalent main group element complexes [44–46]. Some possible structures of this type are depicted in Fig. 3. Homoleptic transition metal hydrometalate structures with metal coordination numbers below 6 and an 18-electron configuration such as square pyramidal CoH_5^{4-} and tetrahedral CoH_4^{5-} and NiH_4^{4-} cannot be formed using a six-orbital sd^5 manifold and 3c-4e bonds and thus necessarily must use some transition metal p-orbitals.

Solid state ternary hydrides with relatively low metal formal oxidation states frequently have magnesium as the counterion. Alternative formulations of the magnesium counterions as Mg_2^{2+} rather than the more usual Mg^{2+} lead to higher formal oxidation states for the transition metal while still providing reasonable chemical bonding models for the hydrometalate anion using the six-orbital sd^5 manifold without p-orbitals and with 3c-4e bonding [37]. In some of the solid state ternary hydrides with the lowest transition metal formal oxidation states (e.g. Ru(0) in Mg_2RuH_4 and Ir(− III) in Mg_4IrH_5) relatively short Mg–Mg distances below 3.0 Å provide some experimental evidence for such models with Mg_2^{2+} rather than Mg^{2+}. If the magnesium counterions are assumed to be Mg_2^{2+} then the hydrometallate anions in Mg_3RuH_3 and Mg_4IrH_5 are the T-shaped RuH_3^{3-} and IrH_3^{2-}, respectively, isoelectronic with PdH_3^- in Fig. 3 and the hydrometallate anion in Mg_2RuH_4 is the sawhorse RuH_4^{2-} isoelectronic with RhH_4^- in Fig. 3. The rather unusual formulation of magnesium counterions as Mg_2^{2+} rather than Mg^{2+} has been justified by the electroneutrality principle, namely avoiding high negative charges on hydrometalate anions such as RuH_4^{4-} and particularly IrH_3^{6-} [37].

3. A survey of homoleptic transition metal hydride structures

3.1. Mononuclear hydrometalates with 18-electron structures

The most common group of homoleptic transition metal hydrides consists of anionic hydrometalates with the 18-electron favored rare gas electronic configura-

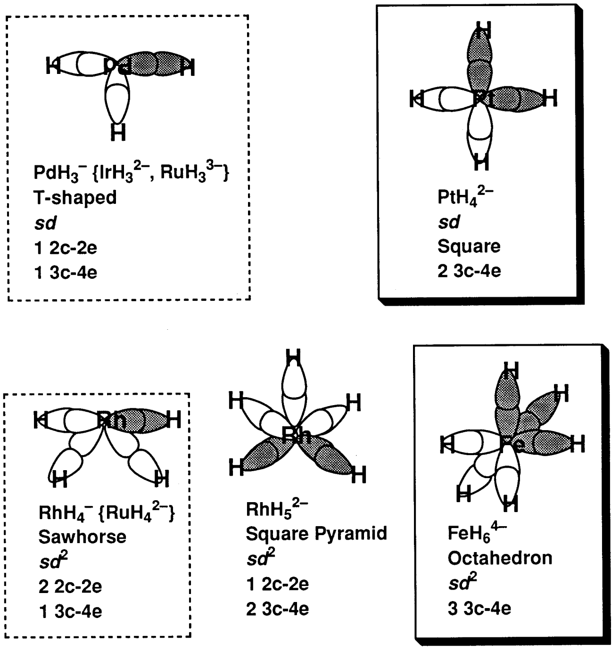


Fig. 3. Three-center four-electron bonding in transition metal hydride structures, where p-orbital participation is not required. The structures that have been found experimentally, namely PtH_4^{2-} and FeH_6^{4-}, are enclosed in solid boxes. Structures found experimentally in ternary magnesium transition metal hydride structures if the magnesium counterions are formulated as Mg_2^{2+} rather than the usual Mg^{2+}, namely IrH_3^{2-} in Mg_4IrH_5, RuH_3^{3-} in Mg_3RuH_3, and RuH_4^{2-} in Mg_2RuH_4, are enclosed in dashed boxes.

tion which are known in a variety of metal formal oxidation states as well as for all of the transition metals from manganese to nickel (Table 1). Many of these 18-electron homoleptic hydrometalates are colorless when pure in accord with their closed shell electronic configurations. Some further information on the hydrometalates listed in Table 1 are given below.

3.1.1. *Manganese, technetium, and rhenium*

The species Mg_3MnH_7, obtained by reaction of MgH_2 with Mn powder in a 3:1 mole ratio with H_2 at 800°C/20 000 atm has been shown by neutron diffraction on the analogous Mg_3MnD_7 to be $(Mg^{2+})_3(MnH_6^{5-})(H^-)$ [47]. The octahedral MnH_6^{5-} contains the d^6 ion Mn(I) and is closely analogous to the octahedral complexes $Mn(CN)_6^{5-}$ and $Mn(CO)_6^+$. The corresponding gray rhenium compound, Mg_3ReH_7= $(Mg^{2+})_3(ReH_6^{5-})(H^-)$ has been obtained by reaction of a mixture of Mg and Re powders with H_2 at 510–520°C/120–155 atm [48].

The soluble enneahydrorhenate ReH_9^{2-} containing formally Re(VII) as in the well-known ReO_4^- is discussed above (Section 2.1). Since the original definitive determination of the structure of ReD_9^{2-} in K_2ReD_9 [21], the ReH_9^{2-} anion has been structurally identified in $BaReH_9$ [49], $KNaReH_9$ [50]), and Rb_3ReH_{10}=$(Rb^+)_3$-$(ReH_9^{2-})(H^-)$ [51]. The structure of K_2ReH_9 has recently been confirmed by a more accurate structure redetermination using neutron diffraction [52].

3.1.2. *Iron, ruthenium, and osmium*

The five-coordinate ion RuH_5^{5-} containing d^8 Ru(0) is found in rusty brown Mg_3RuH_6=$(Mg^{2+})_3(RuH_5^{5-})(H^-)$, obtained by reaction of a mixture of Mg or MgH_2 and Ru powder with H_2 at 78°C/90 atm [53]. The square pyramidal structure of RuH_5^{5-} contrasts with the trigonal bipyramidal structures of $M(CO)_5$ (M = Fe, Ru, Os) and may relate to the greater ease of packing a square pyramidal rather than a trigonal bipyramidal RuH_5^{5-} into a solid state structure with the Mg^{2+} and

Table 1
Mononuclear hydrometalates with 18-electron structures[a]

Group 7	Group 8	Group 9	Group 10	Group 11
$Mn^{I}H_6^{5-}$ (Mg_3MnH_7)	$Fe^{II}H_6^{4-}$ (Mg_2FeH_6)	$Co^{-I}H_4^{5-}$ $(Mg_6Co_2D_{11})$, $Co^{I}H_5^{4-}$ (Mg_2CoH_5)	$Ni^{0}H_4^{4-}$ (Mg_2NiH_4)	$Cu^{I}H_4^{3-}$ $(Ba_7Cu_3H_{17})$
$Tc^{VII}H_9^{2-}$ (K_2TcH_9)	$Ru^{0}H_5^{5-}$ (Mg_3RuH_6), $Ru^{II}H_6^{4-}$ (Mg_2RuH_6)	$Rh^{I}H_5^{4-}$ (Sr_2RhH_5), $Rh^{III}H_6^{3-}$ (Na_3RhH_6)		
$Re^{I}H_6^{5-}$ (Mg_3ReH_7), $Re^{VII}H_9^{2-}$ (K_2ReH_9)	$Os^{II}H_6^{4-}$ (Mg_2OsH_6)	$Ir^{-III}H_3^{6-}$ (Mg_4IrH_5), $Ir^{III}H_6^{3-}$ (Na_3IrH_6)	$Pt^{IV}H_6^{2-}$ (K_2PtH_6)	

[a] An example of a solid state structure containing the hydrometalate ion in question is given in parentheses. Details and literature references are given in the text.

H^- ions. Also a square pyramid, but not a trigonal bipyramid, can be formed using an sd^5 valence orbital manifold without any p-orbitals [30].

The octahedral d^6 M(II) hexahydrometallates MH_6^{4-} (M = Fe, Ru, Os) appear to be very stable and are known in the soluble yellow derivative $FeH_6Mg_4X_4(C_4H_8O)$ (Section 2.1) [27] as well as in solid state species of a variety of stoichiometries including Mg_2FeH_6 [54], $M_2^{II}MH_6$ (M^{II} = Mg, Ca, Sr, Eu; M = Fe, Ru, Os) [55], $SrMg_2FeH_8$=$(M^{2+})(Mg^{2+})_2(FeH_6^{4-})(H^-)_2$ (M = Sr [56], Ba [57], Eu [57]), $Ca_4Mg_4Fe_3H_{22}$=$(Ca^{2+})_4(Mg^{2+})_{4-}(FeH_6^{4-})_3(H^-)_4$ [58], $Yb_4Mg_4Fe_3H_{22}$=$(Yb^{2+})_4(Mg^{2+})_4(FeH_6^{4-})_3(H^-)_4$ [59], $LiMg_2RuH_7$=$(Li^+)(Mg^{2+})_2(RuH_6)^{4-}(H^-)$ [60], $LiMg_4Os_2H_{13}$=$(Li^+)(Mg^{2+})_4(OsH_6^{4-})_2(H^-)$ [61], and $BaMg_2MH_8$=$(Ba^{2+})(Mg^{2+})_2(MH_6^{4-})(H^-)_2$ (M = Ru, Os) [62]. The MH_6^{4-} anions (M = Fe, Ru, Os) are isoelectronic with the very stable cyano complexes $M(CN)_6^{4-}$ (M = Fe, Ru, Os) [3].

3.1.3. Cobalt, rhodium, and iridium

The 18-electron square pyramidal anion CoH_5^{4-} containing formally Co(I) is found in several solid state derivatives including black Mg_2CoH_5 [63–66] and $M_4Mg_4Co_3H_{19}$=$(M^{2+})_4(Mg^{2+})_4(CoH_5^{4-})_3(H^-)_4$ [67]. The analogous RhH_5^{4-} is found in M_2RhH_5 (M = Ca [68] and Sr [69]). The species $Mg_6Co_2D_{11}$=$[(Mg^{2+})_{24}(Co^{I}D_5^{4-})_2(Co^{-I}D_4^{5-})_6(D^-)_{10}]_{1/4}$ contains not only square pyramidal CoD_5^{4-} but also the four-coordinate ion CoD_4^{5-} containing formally Co(− I) isoelectronic with the well-known $Co(CO)_4^-$. The structure of the CoD_4^{5-} ion in $Mg_6Co_2D_{11}$ is described as 'saddle shaped' and may be readily be derived from the expected tetrahedral structure by relatively minor distortions arising from packing in the solid state structure.

Standard ternary solid state hydride synthetic methods for the heavier metals of this group readily give the octahedral $M^{III}H_6^{3-}$ (M = Rh and Ir) containing the d^6 M(III) analogous to the very stable hexacyanometalates, $M(CN)_6^{3-}$ (M = Rh, Ir) [3]. Thus the colorless hydrides $M_3^IMH_6$ (M^I = Li, Na; M = Rh, Ir) are readily obtained by reactions of the alkali metal hydride with the powdered noble metal at 360–500°C under H_2 pressure [70,71]. The analogous CoH_6^{3-} analogous to the very stable $Co(CN)_6^{3-}$ [3] appears to be unknown in accord with the greater stabilities of higher metal oxidation states for the heavier transition metals in a given column of the periodic table.

An example of a very low formal apparent oxidation state in a homoleptic hydrometalate occurs in dark gray Mg_4IrH_5, obtained by reaction of Mg and Ir powders with H_2 at ~ 500°C/40–100 atm [12]. This compound can be formulated as $(Mg^{2+})_4(IrH_3^{6-})(H^-)_2$ containing formal Ir(− III) in the IrH_3^{6-} anion, which has the favored 18-electron rare gas configuration and is isoelectronic with the known superreduced metal carbonyl anions $M(CO)_3^{3-}$ (M = Co, Rh, Ir) [72]. However, some short Mg–Mg distances in Mg_4IrH_5 (as short as 2.754 Å) suggest an alternative formulation as $(Mg_2^{2+})_2(IrH_3^{2-})(H^-)_2$ containing an Ir(I) anion IrH_3^{2-} with the iridium atom in the more usual + 1 oxidation state and ideal T-shaped geometry with one 2c-2e Ir–H bond and one 3c-4e H–Ir–H bond isoelectronic with PdH_3^- depicted in Fig. 3.

3.1.4. Nickel, palladium, and platinum

The tetrahedral NiH_4^{4-}, containing formally Ni(0) analogous to the well-known $Ni(CO)_4$, is found in the red-brown species Mg_2NiH_4 [73–77]. Because of the ease of formation of Mg_2NiH_4 from an Mg_2Ni alloy and H_2 at elevated temperatures analogous to the facile formation of $Ni(CO)_4$ from Ni metal and CO at atmospheric pressure, an Mg_2Ni alloy has been used as a hydrogen storage material [78]. The tetrahedral NiH_4^{4-} is also found in quaternary materials of the type $M^{II}MgNiH_4$ ($M^{II} = Ca$ [79,80], Sr [81], Yb [81], and Eu [81]).

No 18-electron homoleptic hydropalladates appear to be known despite the abundance of palladium hydrides of other types. In the case of platinum the colorless octahedral PtH_6^{2-} with d^6 Pt(IV) is known in M_2PtH_6 ($M = Na$ [82], K [83], Rb [84], Cs [84]), obtained by reactions of the alkali metal hydrides with Pt sponge with H_2 at 500°C/1500 atm. The anion PtH_6^{2-} is analogous to the well-known octahedral $PtCl_6^{2-}$.

3.1.5. Copper, silver, and gold

The 18-electron tetrahedral copper(I) hydride anion CuH_4^{3-} is found in $Ba_7Cu_3H_{17}=(Ba^{2+})_7(CuH_4^{3-})_3(H^-)_5$ obtained from the reaction of Ba/Cu alloys with H_2 under pressure [85]. No homoleptic hydrometalates of silver or gold appear to have been characterized.

3.2. Hydrometalates with 16-electron structures

3.2.1. Square planar derivatives

A variety of d^8 transition metals form 16-electron square planar complexes. Hydrometalates of this type include the Rh(I) derivative RhH_4^{3-} in Li_3RhH_4 [77]; the Pd(II) derivative PdH_4^{2-} in $M_2^IPdH_4$ ($M = Na$ [86], Rb [87], Cs [87]) and $M_3^IPdH_5=(M^+)_3(PdH_4^{2-})(H^-)$ ($M = K$ [88], Rb [88], Cs [88]) the Pt(II) derivative PtH_4^{2-} in $M_2^IPtH_4$ ($M = Na$ [89,90], K [91,92], Rb [93], Cs [93]) and $M_3^IPtH_5=(M^+)_3(PtH_4^{2-})(H^-)$ where $M = K$, Rb, Cs [94]. Two square planar PtH_4^{2-} units are linked by a hydride bridge in the isolated $Pt_2H_9^{5-}$ ions found in $Li_5Pt_2H_9$ [95].

3.2.2. The anomaly of RuH_4^{4-}

The apparent 16-electron anion RuH_4^{4-} containing the d^8 Ru(0) as found in dark red Mg_2RuH_4, obtained from the reaction of a mixture of Mg and Ru with H_2 at 780°C/160 atm [96], might likewise be expected to be a square planar derivative. However, examination of its structure by X-ray and neutron diffraction [96] reveals a non-planar sawhorse for the RuH_4^{4-} anion, which can be derived from an octahedron by removal of two ligands in relative *cis*-positions. A closer examination of this structure reveals that these otherwise vacant positions are connected to adjacent RuH_4^{4-} units through Ru–Ru bonding to form a zigzag chain (Fig. 4) with an Ru–Ru distance of 3.236(4) Å. Thus, the Ru/H subnetwork in Mg_2RuH_4 does not consist of discrete mononuclear RuH_4^{4-} anions but an infinite bonded chain of Ru atoms with 4 H atoms bonded to each Ru atom. Since each Ru atom in Mg_2RuH_4 is bonded to two other Ru atoms as well as the four H atoms in the polymeric anion $[RuH_4^{4-}]_\infty$, each Ru atom in this structure is effectively six-coordinate with an 18-electron configuration rather than four-coordinate with a 16-electron configuration; hence the butterfly rather than square planar structure for each RuH_4^{4-} unit. Alternatively the formal oxidation state of the ruthenium atom in Mg_2RuH_4 becomes the common Ru(II) if the magnesium counterions are considered to be Mg_2^{2+} leading to $(Mg_2^{2+})(RuH_4^{2-})$ in which the RuH_4^{2-} anion is isoelectronic with RhH_4^- with two 2c-2e bonds and one 3c-4e bond (Fig. 3). The minimum Mg–Mg distance in Mg_2RuH_4 is reported to be 2.930(5) Å [96]. The electronic structure of Mg_2RuH_4 is discussed in detail by Miller et al. [97].

3.2.3. Trigonal planar PdH_3^{3-}

Another possible coordination for a toroidal sp^2d^5 manifold is trigonal planar (Fig. 2(b)). This coordination occurs for the d^{10} Pd(0) in the PdH_3^{3-} anion found in ruby red $NaBaPdH_3$, obtained by reaction of NaH, BaH_2, and Pd with H_2 at 450°C/50 atm [98].

3.2.4. Octahedral ReH_6^{3-}

In addition to the 18-electron species ReH_6^{-5}, formally containing Re(I), and ReH_9^{2-}, formally containing Re(VII) (Section 3.1.1), rhenium also forms the 16-electron Re(III) species ReH_6^{3-} in olive green K_3ReH_6, obtained by reaction of KH and Re powder with H_2 at 580°C/3000 atm [99]. X-ray and neutron diffraction studies indicate a regular octahedral structure for the ReH_6^{3-} anion despite its 16-electron configuration and only weak temperature-independent paramagnetism.

3.3. Other electronic configurations in homoleptic hydrometallates

3.3.1. The linear 14-electron complexes MH_2^{2-} (M = Pd, Pt)

The cylindrical spd^5 manifold (Fig. 2(a)) can form two-coordinate linear structures in 14-electron complexes of d^{10} metals. In homoleptic hydrometalate chemistry the Pd(0) anion PdH_2^{2-} is an example of such a species and is found in Na_2PdH_2 [100], $LiSr_2PdH_5$=$(Li^+)(Sr^{2+})_2(PdH_2^{2-})(H^-)_3$ [101], and $CaPdH_2$ [102]). The complexes M_3PdH_3 (M = K [103] and Rb [104]) are not $(M^+)_3(PdH_3^{3-})$ with trigonal Pd(0) but instead $(M^+)_3(PdH_2^{2-})(H^-)$ with linear Pd(0) indicating instability of PdH_3^{3-} towards hydride dissociation to give PdH_2^{2-} (Section 3.2.3). More

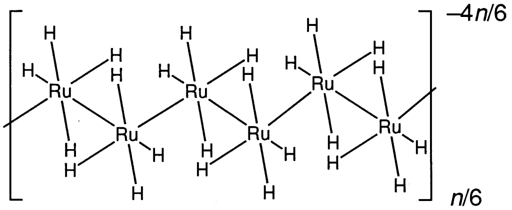


Fig. 4. The infinite zigzag (*cis*-divacant octahedral) $[RuH_4^{4-}]_\infty$ subnetwork found in Mg_2RuH_4 showing six of the repeating units.

recently, the corresponding Pt(0) anion PtH_2^{2-} has been found [105] in Li_2PtH_2 obtained by the thermal decomposition of $Li_5Pt_2H_9$ at 220°C under argon.

3.3.2. The Mn(II) derivative MnH_4^{2-}

The tetrahedral MnH_4^{2-} is found in pink $M^I_3MnH_5$=$(M^+)_3(MnH_4^{2-})(H^-)$ where $M^I = K$, Rb, Cs, obtained from the reaction of M^IH and Mn powder with H_2 at 600°C/3000 atm [106]. The d^5 Mn(II) found in MnH_4^{2-} is particularly stable in a high-spin environment because of the half-filled d-orbitals so that the 18-electron configuration is no longer necessarily favored. The magnetic moment of K_3MnH_5 is 6.0 B.M. in accord with the five unpaired electrons expected for Mn(II) in a high-spin tetrahedral environment.

3.3.3. The dinuclear hydroruthenate $Ru_2H_6^{12-}$

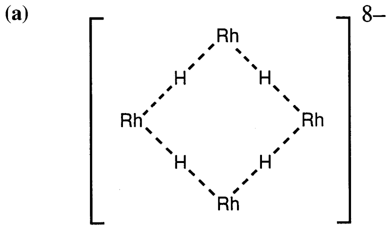
Reaction of a mixture of Mg and Ru powders with H_2 at 600°C/9 atm gives dark gray Mg_3RuH_3 [107], shown by X-ray and neutron diffraction studies to contain the T-shaped RuH_3^{6-} ion apparently containing Ru in the very unusual −3 formal oxidation state However, the RuH_3^{6-} units appear in $Ru_2H_6^{12-}$ dimers with an apparent Ru–Ru bond of 3.31 Å. The Ru atoms thus have the 18-electron rare gas configuration as follows:

Neutral Ru atom	8 electrons
Three neutral hydride ligands: $3 \times 1 =$	3 electrons
Ru–Ru bond:	1 electron
–6 charge:	6 electrons
Electronic configuration of the Ru atom	18 electrons

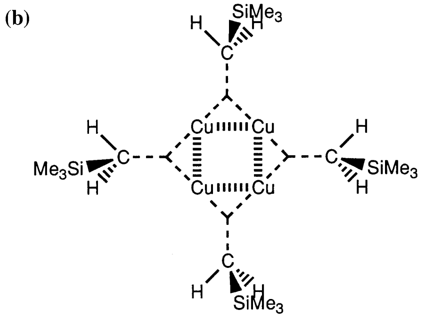
Alternatively the formal oxidation state of the ruthenium atom inMg_3RuH_3 is the more typical zero if the magnesium counterions are Mg_2^{2+} leading to $(Mg_2^{2+})_3(RuH_3^{3-})_2$ in which the RuH_3^{3-} anion is isoelectronic with PdH_3^- with one 2c-2e and one 3c-4e bond. The minimum Mg–Mg distance in Mg_3RuH_3 is reported to be 3.034(5) Å [107]. The electronic structure of Mg_3RuH_3 is discussed in detail by Miller et al. [97].

3.3.4. The polynuclear hydrorhodate $Rh_4H_4^{8-}$

Reaction of a binary MgRh alloy with H_2 at 475°C/130 atm gives a dark gray product of approximate stoichiometry MgRhH, which formally can be considered to contain RhH^{2-} with d^{10} Rh(−I) isoelectronic with Cu(I) [108]. Neutron diffraction of the corresponding deuteride indicates the presence of macrosquare eight-membered Rh_4D_4 rings with 177.5° Rh–D–Rh angles along the edges and 87.5° D–Rh–D angles at the vertices (Fig. 5(a)). The cyclic tetrameric structure of $Rh_4H_4^{8-}$ with formal Rh(−I) is related to the tetrameric structure of alkyls of the isoelectronic Cu(I) such as $Cu_4(CH_2SiMe_3)_4$ (Fig. 5(b)) [109] except for reversal of the positions of the H/C atoms and the Rh/Cu atoms. As a result of this structural difference the structure of $Cu_4(CH_2SiMe_3)_4$ (Fig. 5(b)) incorporates 2e-3c Cu–C–



The $Rh_4H_4^{8-}$ macrosquare in $Mg_4Rh_4H_4$



The tetrameric Cu(I) alkyl $Cu_4(CH_2SiMe_3)_4$

Fig. 5. (a) The $Rh_4H_4^{8-}$ macrosquare found in $Mg_4Rh_4H_4$. (b) The square structure of the tetrameric Cu(I) alkyl $Cu_4(CH_2SiMe_3)_4$.

Cu bonds with linearly coordinated Cu whereas the ‘inverse’ structure of $Rh_4H_4^{8-}$ (Fig. 5(a)) incorporates 2e-3c H–Rh–H bonds with linearly coordinated H. This structural difference might arise from supplementary Cu–Cu bonding in the neutral $Cu_4(CH_2SiMe_3)_4$ (see the hashed lines in Fig. 5(b)) but the lack of analogous Rh–Rh bonding in $Rh_4H_4^{8-}$ because of the negative charge on the Rh atoms.

4. Summary

Transition metal hydride anions of diverse types are found in the structures of solid state ternary and quaternary transition metal hydrides containing electropositive metals such as the alkali and alkaline earth metals. Mononuclear homoleptic hydrometalate anions with the favored 18-electron configuration of the next rare gas are known for transition metals from manganese to copper and some of their heavier congeners and in formal oxidation states ranging from -3 in IrH_5^{6-} found in Mg_4IrH_5 to $+7$ in ReH_9^{2-} found in K_2ReH_9. Soluble homoleptic transition metal hydrometalates are much rarer being limited to MH_9^{2-} ($M = Tc$, Re) in K_2MH_9 and FeH_6^{4-} in derivatives of the type $FeH_6Mg_4X_4(C_4H_8O)$.

Some interesting homoleptic hydrometalates are known in which the central metal actually or apparently violates the 18-electron rule. The late transition metals, particularly Pd and Pt, form homoleptic hydrometalates with 16-electron configurations (e.g. square planar PdH_4^{2-} and PtH_4^{2-} and trigonal PdH_3^{3-}) and even linear 14-electron configurations (e.g. PdH_2^{2-}) analogous to complexes of these metals with other monodentate ligands. However, the apparent 16-electron complex RuH_4^{4-} found in Mg_2RuH_4 does not have the expected square planar configuration but instead forms infinite $[RuH_4^{4-}]_\infty$ chains in which each RuH_4 unit is linked to two adjacent RuH_4 units through Ru–Ru bonds so that each Ru atom actually has the favored 18-electron configuration. The tetrahedral MnH_4^{2-} found in K_3MnH_5 is an example of a high-spin d^5 complex which is particularly stable because of the half-filled d shell. The Ru atoms in the T-shaped RuH_3^{6-} ion found in Mg_3RuH_3 acquire the 18-electron configuration through Ru–Ru bonding to form $Ru_2H_6^{12-}$ dimeric units. The RhH^{2-} anion found in MgRhH forms cyclic tetramers $Rh_4H_4^{8-}$ related to but not directly analogous to the cyclic structures of copper(I) alkyls such as $Cu_4(CH_2SiMe_3)_4$.

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