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$(MnH_9)^{2-}$ salts with high hydrogen contents and unusual bonding: Density functional calculations

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The compounds $BaReH_9$ and K_2ReH_9 are the prototypical members of a family of hydrides described as salts of $(ReH_9)^{2-}$ anions. The structures reflect highly unusual chemistry with short H-H distances and at the same time very high ninefold coordination of Re by hydrogen atoms. This is of interest because of the resulting high hydrogen-to-metal ratios, 4.5 in $BaReH_9$ and 3 in K_2ReH_9. Here we use density functional calculations to investigate possible new members of this family including both Re and Mn compounds. We find that although $SrReH_9$ and $CaReH_9$ have not been synthesized these are very likely to be stable compounds that may be prepared in a similar manner as the Ba analog. We also find that the manganese counterparts, including K_2MnH_9, are also likely to be stable and have thermodynamic properties consistent with requirements for hydrogen storage.

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There is currently strong interest in technologies that can be used to store hydrogen safely as a clean carbon-free fuel.[1–3] These include storage in compressed gaseous form, in cryogenic liquid form, as an adsorbate in high surface-area materials, in chemical hydrides and in metal-hydrogen materials. All these approaches present challenges at present. Storage in high-pressure gaseous form is being actively investigated but faces safety and cost issues (especially for carbon-carbon composites) for many prospective applications. Storage in its liquid form is also problematic; this requires cryogenic tanks and involves a substantial energy penalty in connection with liquefaction. Storage in the form of metal hydrides is a proven technology. The essential difficulty with the use of intermetallic alloys (e.g., $LaNi_5$), which have been extensively studied for hydrogen storage, is that they suffer from their low-weight percent capacity to store hydrogen[4,5] even though the volumetric capacity can be very high (in some cases higher than liquid hydrogen). Attention has therefore turned to low-weight chemical hydrides.[6,7] While this field has seen considerable progress, an ideal material for hydrogen storage has yet to be demonstrated, especially from the point of view of reversible storage. As such, it remains of interest to investigate the chemistry of unusual hydrogen containing materials, especially materials with high hydrogen content.

The complex chemical hydrides of Re have been studied for some time[8–14] and in some of them Re is in the highest-known formal valence of 7. The compounds $BaReH_9$ and K_2ReH_9 are two representative members of such complex hydrides, which are composed of $(ReH_9)^{2-}$ structural units. The ninefold coordination of Re in these compounds is remarkable and was discussed in terms of hybrid orbitals on Re by Pauling.[15] While, the Tc compound, K_2TcH_9 is known,[10] no analogous Mn compounds have been reported. This may reflect the fact that high-valent Mn-VII compounds are generally less stable than the corresponding Re compounds or the stronger Hund's coupling on Mn, which works against the stability of the covalent bonds involving Mn *d* electrons relative to the corresponding Re compounds. The Re-based hydrides are not of practical interest for hydrogen storage not only because Re is heavy ($BaReH_9$ has a weight capacity of only 2.7% even though the hydrogen-to-metal ratio is 4.5) but also because it is extremely expensive, several times more than Pt or Au. Tc is even more expensive than Re and furthermore it is highly radioactive. Understanding whether $(MnH_9)^{2-}$ compounds do not exist because of thermodynamic instability or whether they may exist but have not been discovered because different synthetic routes are required for Mn than Re or Tc is an important question, both from the point of view of gaining insights into the chemistry of these materials and also for potential practical reasons.

As mentioned, the Re salts have highly unusual structures with short H-H distances and high transition-metal coordination. The structure of H_9 coordination cage is a tricapped trigonal prism (see Fig. 1), which is also the stable structure of free 18 *s*-electron clusters, such as Mg_9 and Be_9. The stability of these clusters is associated with an electronic-shell structure, in particular, electronic levels consisting of a low-lying fully symmetric *s*-like state, three *p*-like states, and five *d*-like states, all of which are filled at an electron count of 18. These shells are all derived from combinations of *s* states on the nine atoms and reflect the bonding of the cluster. In our previous work we noted that this can provide an explanation for the stability of $(ReH_9)^{2-}$ anions since the symmetry of the *d*-like cluster states is such that they may form strong radial σ bonds with the Re 5*d* orbitals. This can give a stable 18 valence electron $(ReH_9)^{2-}$ unit with an occupied electronic structure consisting of one *s*-like symmetric bonding level and three *p*-like bonding levels associated with the H-H interaction plus five bonding orbitals of Re *d*—*G d* character, where *G* denotes the H_9 cluster. This picture was shown to be supported by density functional calculations.[18]

In this paper, we use density functional calculations to investigate that additional members of this family based on lighter elements may exist. First of all we investigate replacement of Ba by the lighter alkaline-earth (Ae) elements,

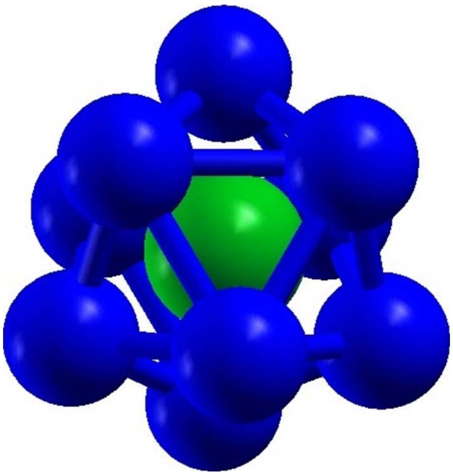

FIG. 1. (Color online) Structure of the $(ReH_9)^{2-}$ anions in $BaReH_9$ emphasizing the H-H bonding. The nine H atoms form a tricapped trigonal prism around Re. This structure is stabilized by H-H bonding and also by σ bonding between Re *d* and cage *d*-like orbitals (see text).

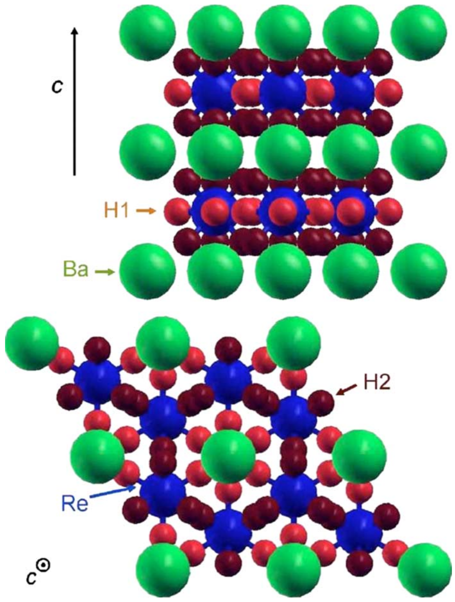

FIG. 2. (Color online) Crystal structure of $BaReH_9$ showing Ba and ReH_9 layers stacked along the *c* axis (top) and the structure of the hexagonal planes (bottom). The H1 and H2 sites are shown by small light and dark red circles, respectively, Ba by large light green spheres, and Re by large dark blue spheres.

Sr and Ca. While this is chemically intuitive, it does move outside the space of known compounds in the sense that Sr and Ca have higher electronegativities than Ba or K, and therefore are somewhat less stabilizing for anionic clusters such as $(ReH_9)^{2-}$ but also have somewhat more stable competing phases (BaH_2 is less stable than SrH_2, which in turn is less stable than CaH_2). Second, we investigate new $(MnH_9)^{2-}$ salts. In our previous work[18] we studied the new compound $BaMnH_9$ finding that it may well exist. The problem with compounds like this is that because the chemistry of Mn is rather different from that of Re, a new effective synthesis route may be necessary to synthesize this compound. With this in mind, it is of value to investigate several potential compounds with different counter ions to find alternate synthesis targets that perhaps have different synthesis routes.

Density functional calculations offer a promising means of understanding and improving the properties of hydrogen-storage materials.[16,17] In our previous paper,[18] we have shown from our *ab initio* local-density approximation (LDA) calculations that the electronic structure and stability of the manganese counterpart, $BaMnH_9$, are quite similar to those of $BaReH_9$ but it raises the weight-percent capacity to nearly 4.5% which is a substantial improvement. Further, manganese is a relatively cheap material. This has encouraged us to perform a systematic study in the series of compounds $AeReH_9$ and $AeMnH_9$, where Ae is an alkaline-earth element, and the results are presented in this paper. The results for the sister compounds K_2ReH_9 and K_2MnH_9 are also presented. As we will show below, these hydrides form a promising new class of complex chemical hydrides for hydrogen storage.

The present calculations were performed within the density functional theory as implemented in the Vienna *ab initio* simulation package (VASP) using projector-augmented pseudopotentials.[19–21] We employed the generalized gradient approximation (GGA) of Perdew and co-workers,[22–24] which is generally more reliable in calculating the formation energies of the hydrides than LDA. An energy cutoff of 650 eV was employed in all of our calculations. The hydride $BaReH_9$ crystallizes in a hexagonal structure (space group $P6_3/mmc$) and consists of alternating triangular layers of Ba and Re stacked along the *c* axis, such that the $(ReH_9)^{2-}$ atoms are at the centers of triangular prisms formed by Ba (see Fig. 2). Each Re is surrounded by three H atoms in its own plane (H1 positions) and six other H atoms (H2 positions) above and below the plane. The H2 atoms form a trigonal prism. Thus, as mentioned, the H atoms are arranged in tricapped trigonal prisms around the Re atoms. The unit cell contains two $(ReH_9)^{2-}$ units, stacked so that the orientation of these units alternates along the hexagonal *c* axis. The crystal structure data for $BaReH_9$ determined by Stetson *et al.*[5] by x-ray diffraction was taken as the starting point in our calculations and the lattice parameters and the internal atomic coordinates were then determined by the total-energy minimization, and these values are given in Table I. Note that the H positions are difficult to determine by x-ray diffraction due to the presence of heavy metal atoms and hence we think that our theoretically determined positions could be taken as reference in future work. The hydrides $SrReH_9$ and $CaReH_9$ have not been synthesized to date but our results shown in Table I indicate that they could be synthesized in the same manner as the Ba compound. The hydride K_2ReH_9 also crystallizes in the hexagonal structure (space group $P62m$) and again consists of $(ReH_9)^{2-}$ units well separated from each other by the K atoms. The crystal structure and atomic positions, including hydrogen sites, for this compound have been determined by neutron diffraction[7] and are given in Table II. The distribution of hydrogen atoms around the Re atoms is the same as in $BaReH_9$, namely, three hydrogen atoms in the

TABLE I. Lattice parameter, a and c (in Å) and the internal atomic coordinates in the space group $P6_3/mmc$ of several Ae-based $AeTH_9$ hydrides calculated in GGA. Here T is either Re or Mn. The coordinates of the atoms are Ba (2a): (0, 0, 0), T(2c): (1/3, 2/3, 1/4), H1(6h): $(x_1, 2x_1, 1/4)$, and H2(12k) $(x_2, 2x_2, z_2)$.

Hydride	a	c	x_1	x_2	z_2
$BaReH_9$	5.1858	9.5398	0.1472	0.4680	0.1230
$SrReH_9$	5.1354	9.3054	0.1446	0.4695	0.1199
$CaReH_9$	5.1202	9.0856	0.1436	0.4699	0.1165
$BaMnH_9$	4.8114	9.2117	0.1519	0.4685	0.1350
$SrMnH_9$	4.9595	8.9149	0.1555	0.4635	0.1286
$CaMnH_9$	4.9041	8.6815	0.1525	0.4649	0.1248

plane of Re and three each above and below the plane. The mean Re-H hydrogen distance is ~1.70 Å. The H-H distances are short in these compounds, ~2 Å, and hence the direct H-H interactions play an important role in the stability of these compounds. These distances are similar to those in $BaReH_9$—a fact that is consistent with the similar nature of the bonding in the two compounds. The crystal structures of the Mn counterparts are not available since they have not been synthesized to date and hence these crystal structures were determined by the total-energy minimisation, starting from the crystal structure data for the Re-based compounds, by relaxing both the lattice parameters and the internal atomic coordinates. These results are summarized in Table I for the $AeMnH_9$ compounds and in Table II for K_2ReH_9 and K_2MnH_9. We note an excellent agreement between the calculated lattice parameters and atomic coordinates for K_2ReH_9 with the experimental data determined by neutron diffraction.[7] It is interesting to note from Tables I and II that while the lattice parameters for the Mn-based compounds are smaller than those for the Re-based compounds reflecting the smaller ionic radius of the Mn ion relative to that of Re, the internal atomic coordinates are nearly the same in all Mn-based compounds as in the Re compounds, and no dramatic deviations are observed. The similarity of the relaxed structure of the H cages around Mn atoms with that around Re atoms suggests that the bonding is similar in these hydrides. This indicates that the Mn-based compounds are very good candidates for crystallizing in the structures corresponding to Re.

TABLE II. The lattice parameters, a and c (in Å) and the internal atomic coordinates in the space group $P\bar{6}2m$ of K_2ReH_9 and K_2MnH_9. The coordinates of atoms are Re1 (Mn1) at $1a(0,0,0)$, Re2 (Mn2) at $2d(1/3,2/3,1/2)$, K1 at $3f$ $(x1,0,0)$, K2 at $3g(x2,0,1/2)$, H1 at $3f(x3,0,0)$, H2 at $6i(x4,0,z4)$, H3 at $6k(x5,y5,0)$, and H4 at $12l(x6,y6,z6)$.

	K_2ReH_9		K_2MnH_9
	Experimental	Calculated	Calculated
a	9.599	9.5972	8.9503
c	5.549	5.5958	5.2017
$x1$	0.5876	0.5901	0.5900
$x2$	0.2626	0.2613	0.2617
$x3$	0.1749	0.1766	0.1710
$x4$	0.8712	0.8723	0.8766
$z4$	0.2077	0.2138	0.2047
$x5$	0.1441	0.1404	0.1455
$y5$	0.6314	0.6248	0.6261
$x6$	0.2337	0.2264	0.2302
$y6$	0.5321	0.5300	0.5347
$z6$	0.7195	0.7208	0.7139

The electronic structure and other related properties of $BaReH_9$ and $BaMnH_9$ compounds were discussed in detail in our previous work.[18] All of these hydrides are large band-gap insulators. As mentioned, the electronic structure of these compounds is determined mainly by the interaction between the H_9 cages and the TM (TM=Re and Mn) atoms. This interaction is covalent in nature and is unusual due to the occurrence of H_9 cages. The details of this unusual bonding have been discussed in our previous paper.[18] The band gaps are due to the energy difference between bonding and antibonding Re/Mn d—G d orbitals. The band gaps in the Mn compounds are somewhat smaller than in the Re compounds since the 3d orbitals in Mn are less extended than the 5d orbitals of Re, yielding somewhat lower bonding-antibonding splittings. The Ae and K atoms act essentially as electron donors. We focus here mainly on the stability of various hydrides, which is of direct interest for hydrogen-storage applications. The enthalpies of formation of several alkaline-earth-based Re and Mn hydrides, calculated with respect to the elements in their relevant metallic states (with Mn in the antiferromagnetic configuration), and the H_2 molecule, are given in Table III. The results for K_2ReH_9 and K_2MnH_9 are also given in Table III. The calculated formation energies of $BaReH_9$, $SrReH_9$, and $CaReH_9$ are found to be −68.3, −64.4, and −51.3 kJ/mol H_2, respectively. This shows that while the latter two compounds have not yet been synthesized, they have stabilities of the same order as the Ba analog since they all three have the structural cagelike arrangements of hydrogen atoms around Re atoms. As one goes from Ba to Ca, there is a decrease in the cell volume due to smaller ionic radii of the elements involved, and furthermore there is a trend toward lower stability with increasing Ae electronegativity. We also note that these enthalpies of formation are all less negative than those for the binary hydrides; namely, −149.3, −166.0, and −174.4 kJ/mol H_2

TABLE III. The enthalpies of formation ΔH_f (in kJ per H_2 molecule) of several Ae-based AeTH_9 hydrides, where T is either Re or Mn, calculated in GGA with respect to the elements in their relevant metallic states. The negative sign indicates the stability of the corresponding hydride. The enthalpies of formations for the hydrides K_2ReH_9 and K_2MnH_9 are also given at the end. In the last column are given the enthalpies of formation ΔH (in kJ/mol H_2) with respect to the relevant binary hydrides.

Hydride	ΔH_f (kJ/mol H_2) (with respect to elements)	ΔH (kJ/mol H_2) (with respect to binary hydrides)
$BaReH_9$	−68.3	−45.1
$SrReH_9$	−64.4	−35.4
$CaReH_9$	−51.3	−16.1
$BaMnH_9$	−42.2	−11.6
$SrMnH_9$	−43.9	−9.0
$CaMnH_9$	−34.7	+5.3
K_2ReH_9	−71.4	−68.2
K_2MnH_9	−41.3	−29.4

for BaH_2, SrH_2, and CaH_2, respectively. Indeed, these are nearly one-third the values of the binary hydrides and this points out the destabilizing role of the H_9 cluster.

As mentioned, the Mn-based hydrides are of greater interest. From Table III, we notice that the enthalpies of formations of the three hydrides, $BaMnH_9$, $SrMnH_9$, and $CaMnH_9$ are all negative, and fall in the range of ~−40 kJ/mol H_2. They are less negative than the corresponding Re-based compounds due to the reduced covalency associated with the less-extended Mn d orbitals. However, the fact that these compounds are stable is encouraging and merits further experimental investigation. We note that on the one hand the structure may be more complex than those we considered. If this is the case the formation enthalpies will be more negative, which will make the synthesis more likely. On the other hand, there may be unanticipated competing phases that will work in the opposite direction. The phase diagrams of the ternary hydrides can be quite complex and is beyond the scope of this paper.

The compounds K_2ReH_9 and the new proposed K_2MnH_9 also have the H_9 cages and similar $(ReH_9)^{2-}$ units. Despite the fact that there are two K atoms in these hydrides, they are still of interest since the atomic weight of K is relatively low considering the high H-to-metal ratio. From Table III, one may note that the calculated enthalpies of formations for these compounds of, −71.4 and −41.2 kJ/mol H_2, are promising although, as expected, the Re-based hydride again has a more negative value. The hydride K_2MnH_9 is of considerable interest since, as shown in Table II, it has an H_9 cage structure identical to that of its sister compound K_2ReH_9. There is only a volume reduction due to the ionic size. Further, its enthalpy of formation is quite close to that of PdH and thus falls within the range of practical applications. The enthalpy of formation of K_2ReH_9 is, on the other hand, only slightly less negative than that of KH, −82.8 kJ/mol H_2, and this makes this compound very stable.

We note that these calculations do not include the contributions from the zero-point energy. Generally, zero-point energy changes hydride enthalpies of formation by less than 20 kJ/mol H_2. The calculation of the zero-point energy requires a knowledge of the full vibrational spectrum (and in addition there are anharmonic corrections). In the present compounds, there is a strong covalent bonding involving H_9 cages, which suggests high vibrational frequencies. In our previous study of $BaMnH_9$ within the LDA three full symmetry phonon frequencies were reported. While this is too few to obtain a reliable zero-point energy, the shear mode (with respect to the H-Re bond) was at ~900 cm^{-1} and the average of two stretch modes was ~1970 cm^{-1}. Based on this a rough estimate of the average phonon frequency is ~1250 cm^{-1}. This is greater than 1/6 of the bond-stretch frequency of the H_2 molecule (~700 cm^{-1}) implying that the zero-point contribution is destabilizing in these compounds by perhaps no more than 20 kJ/mol.H_2. But this is only a rough estimate.

The occurrence of the H_9 cages and short H-H distances within the cage clearly plays a central role in the decomposition reaction which may proceed directly via the elements and hydrogen molecules, and not through the formation of binary hydrides. However, we note that all the hydrides presented in this paper are also stable with respect to the binary hydrides since the enthalpies of formations calculated with respect to the relevant binary hydride, and shown in Table III, are although less negative but nevertheless negative, except for $CaMnH_9$ for which it is marginally endothermic, ~+5 kJ/mol H_2. The best result is obtained for K_2MnH_9 for which we find a value of −29.4 kJ/mol H_2 with respect to KH. This value is quite close to the one found for PdH. With these less negative values one might conclude that the decomposition of these hydrides might follow through the formation of binary hydrides. It is important in this connection to keep in mind the recent work[25] on the destabilization of MgH_2 by the addition of, for example, Ti that leads to the formation of a new hydride Mg_7TiH_{16} with a crystal structure and the arrangement of hydrogen atoms different from that found in MgH_2. The electronic-structure calculations[26] show that this hydride is stable with respect to the metallic elements but not with respect to the binary hydrides MgH_2 and TiH_2. This hydride has, nonetheless, been prepared under pressure. This again brings to attention the crucial role of H_9 cages.

In conclusion, we have proposed hydrides with H_9 cages and Re/Mn at the centers of the cages. The bonding in these hydrides is unusual since the interaction between the hydrogen atoms and the transition-metal atom does not occur directly but through these cages. These compounds present interesting properties for hydrogen storage. It will be of interest to investigate experimentally whether any of these compounds can be made and what their properties are.

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