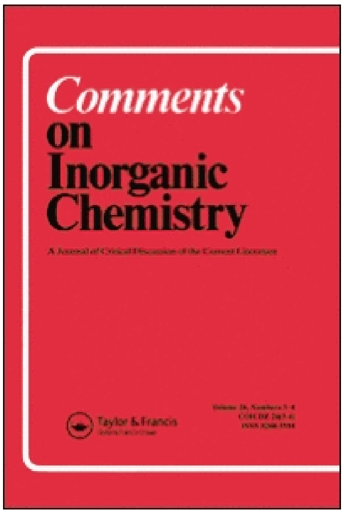


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Prediction of Nonclassical Hydrogen Complexes of Nontransition Metals

Cleanthes A. Nicolaides[a]; Emmanuel D. Simandiras[a]
[a] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

To cite this Article Nicolaides, Cleanthes A. and Simandiras, Emmanuel D.(1996) 'Prediction of Nonclassical Hydrogen Complexes of Nontransition Metals', Comments on Inorganic Chemistry, 18: 2, 65 — 75
To link to this Article: DOI: 10.1080/02603599608032714
URL: http://dx.doi.org/10.1080/02603599608032714

Prediction of Nonclassical Hydrogen Complexes of Nontransition Metals

CLEANTHES A. NICOLAIDES and
EMMANUEL D. SIMANDIRAS
Theoretical and Physical Chemistry Institute,
National Hellenic Research Foundation,
48, Vas. Constantinou Ave.,
116/35 Athens, Greece

Received June 10, 1995

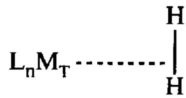
In the past few years, theoretical and computational work, including the effects of electron correlation, allowed the prediction of nonclassical hydrogen complexes of nontransition metals. In this Comment, these results are connected to others, starting with H_3^+, and a review of the "nonclassical" binding features of molecular H_2 to metals and nonmetals is given. As an example, the prediction of the structure of a new such complex, the $Li_4H_2^{2+}$, is made.

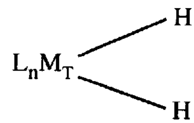
I. INTRODUCTION

Recent reviews[1–6] have presented and discussed the remarkable progress that has occurred during the past decade in the field of nonclassical hydrogen complexes (NCHC's) of *transition metal* compounds. The field took off after a report by Kubas *et al.*[7] on the experimental finding that the hydrogen molecule may bind on a transition metal

Comments Inorg. Chem.
1996, Vol. 18, No. 2, pp. 65–75
Reprints available directly from the publisher
Photocopying permitted by license only

M_T in molecular from as in (1) rather than as in the atomic form of the classical dihydrides (2)





(1) (2)

L_n represents ligands to which the transition metal atom is bound. In (1) the frequency of the H–H vibration is shifted from that of free H_2 (4400 cm^{-1}) and is a useful factor in the determination of the structure (see, for example, the discussion in ref. 6). In (2), it is the M_T–H frequencies that are measured, while the hydrogen σ bond is broken. (The equilibrium internuclear distance for the free H_2 is $R_o = 1.40$ a.u. $= 0.74$ Å).

The discussions in refs. 1–6 lead to the conclusion that part of the enthusiasm of the inorganic chemists for this field is due to the fact that structures like (1) were unexpected. For example, in his concluding section, Kubas[1] states "*significantly, coordination of a H–H bond represents the first stable intermolècular interaction to a sigma bond with a metal center. Few, if any, researchers would have believed that H_2 complexes would be stable relative to free H_2 or metal hydrides.*"

Although transition metal atoms with their characteristic d electrons have attracted this special attention, it turns out that NCHC's also exist for light nontransition metals (see below) as well as for *light nonmetals* such as BH_5,[8] CH_5^+,[9] SiH_5^+[10a] and GeH_5^+.[10b] The accurate experimental determination has come only very recently in two cases, BH_5[11] and CH_5^+,[12] using molecular beam or matrix isolated infrared spectroscopy. In both cases this experimental characterization has been possible only because of the existence of high accuracy theoretical calculations that were extensively used in the design of the experiments and the interpretation of the IR data. It is interesting to note that for the vibrational spectra of CH_5^+, the stabilization necessary for the spectral measurments was achieved by formation of a weak cluster with the hydrogen molecule,[12] i.e., a NCHC bound by 40 kcal/mol is intermolecularly bound to another H_2 molecule by ~ 1 kcal/mol. The H–H stretching bands for a similar complex of Si, SiH_7^+ have also been determined spectroscopically.[13]

The purpose of the present Comment is twofold: First, to bring to attention the fact that NCHC's also exist for compounds whose central atoms are *nontransition metals* (e.g., Li, Be, Mg, Al), suggesting that the reasons for their occurrence lie beyond the specific properties of the outer d-electrons of the transition metals and may be similar to those involving light nonmetals. These reasons seem to be conditions of electron deficiency and charge-induced polarization of the H_2 σ bond and of some participation in back-bonding between the HOMO-LUMO atom orbitals and the antibonding σ^* orbital of H_2. Second, to show that, since NCHC's are also found in metal containing compounds of small sizes, e.g., $OBeH_2$, geometry-optimization computations including electron correlation can be carried out so as to acquire reliable information as to their structure and properties. It is reasonable to expect that by realizing that there is a number of atoms other than the transition metals which, under certain conditions, bind H_2 in molecular form (in absolute or in local minima of the potential energy surface), interest in new directions in the synthesis of complexes of hydrogen or of other strong σ bonds (such as CH_4) could be developed.

It should be stressed that although theoretical predictions of molecular structure and stability might have lower accuracy than measurements, when such are made, they can give useful guidelines towards the design, the synthesis and the characterization of novel compounds, as well as a very good understanding of the chemical binding involved. It is also noted that although some H_2 complexes of nonmetals have been detected experimentally, to our knowledge no such data exist for NCHC's of nontransition metals, except for the binding energies measured for Na^+ and K^+ clusters with H_2.[14]

II. CALCULATIONS AND RATIONALIZATION OF NCHC's OF TRANSITION METALS

The experimental characterization of the first NCHC's of transition metals was soon verified by ab initio calculations on η_2-bonded H_2-$W(CO_3)(PH_3)_2$ carried out by Hay.[15] Hay's calculation was at the Hartree–Fock level with a relativistic effective core potential for W. His results on the stability of this compound were interpreted in terms of σ bonding and π back-bonding involving occupied and unoccupied metal d-orbitals and the σ and σ^* orbitals of H_2. Hay also related the electron-withdrawing or electron-donating characteristics of the ligands to the effectiveness of the oxidative addition of H_2. Calculations at the extended Hückel level and molecular orbital analyses aiming at rationalizing the formation of such compounds were also carried out by several groups.[5,16–19]

Although approaches at the molecular orbital level may provide some insight into the molecular structure of these compounds, the fact remains that when electron correlation is present (for the heavy metals relativistic effects are present as well at the orbital level), in order for the study of molecular structure and spectroscopy and of properties such as relative energies of isomers or heats and paths of formation or dissociation of molecules to be reliable, advanced ab initio calculations must be carried out. In fact, the first serious calculations on the reaction of H_2 with transition metals showing the existence of the formation of a NCHC were published in 1983–84 by Siegbahn's group[20,21] apparently independently of Kubas' experimental work. Using the configuration–interaction (CI) method, they studied the interaction of H_2 with Ni and Pd in the compounds NiH_2, PdH_2, $Ni(CH_3)_2H_2$ and $Pd(H_2O)_2H_2$. They found that PdH_2, where the free atom configuration is d^{10}, is a weakly bound hydrogen complex. However, "*the addition of water ligands to Pd lowers the atomic d^9's configuration relative to the ground state and thus facilitates sd hybridization. This results in the formation of covalent Pd–H bonds and the complete splitting of the H–H bond in $(H_2O)_2PdH_2$.*"

III. FORMATION OF NCHC's WITH ATOMS OTHER THAN TRANSITION METALS

In recent years, theoretical work carried out in this institute has provided information about the formation of NCHC's of nontransition metals.[22–28] This work had its beginning in the molecule BeH_2^{2++} and in our interest in establishing the existence of ground surfaces of polyatomic species which are repulsive, except for a stable (upon geometrical distortions) local minimum lying *above* the energies of dissociation products. Molecules in such states contain usable energy.[29–31] Upon the recommendation of the referee of Ref.,[22] we made the connection of the unusual bonding properties of BeH_2^{2++} with the findings about the NCHC's of transition metals, as presented in Refs. 2 and 3 and references therein. Soon afterwards the results on the formation, stability and isomers of $OBeH_2$ were published.[23,32]

Our continuing interest in designing and computing new inorganic molecules with the property of a NCHC has led us to the recognition that species where H_2 is linked to a "central" atom in molecular form were already predicted earlier for simple molecules and clusters and that, therefore, this property is by no means an exclusive feature of compounds of transition metals.

We start with H_3^+, whose structure we consider to have some prototypical features relevant to our discussion. This is the simplest NCHC and is formed by the protonation of H_2, i.e., $H_2 + H^+ \rightarrow H_3^+$. As a result of attractive electrostatic interactions and electron deficiency, H_3^+ binds with respect to $H_2 + H^+$ already at the SCF level (e.g., Ref. 33). Its geometry is that of an equilateral triangle, where the H–H distance is 1.65 a.u.,[33] reasonably close to that of the free H_2 (1.40 a.u.). An interesting feature of its potential energy surface (PES) is that as the side of the H_3^+ triangle, R, is increased, the ^1A curve corresponding to $H_2 + H^+$ rises above the $H_2^+ + H$ curve at about 2.5 a.u.[34] The phenomenon of avoided or of conical intersections between the lowest PES's occurs in many singly ionized molecules. It also occurs in dications, for example, in the NCHC of BeH_2^{++}.[22] Understanding quantitatively such characteristics of the PES's—either in the adiabatic or in some quasiadiabatic representation—reveals the essentials of the energetics and of the low-energy spectroscopic properties of molecules.

How can one make heuristic predictions of possible new hydrogen complexes? Our approach has been to first understand the nature of bonding occurring when positively charged metal or nonmetal ions interact with H_2. The related properties (e.g., geometry, vibrational frequencies) are obtained from extensive geometry-optimized calculations. For example, results for H, Li and Be are given in Table I, obtained from second-order Moller–Plesset (MP2)[35] calculations with very large basis sets.[36] Using this type of extensive calculation as a benchmark, we investigate possible candidates for larger molecular NCHC's involving Li and Be.

Both Li and Be bind H_2 in charged species, as can be seen from Table I. These represent true NCHC's as the H–H bond length in

TABLE I

Structures, harmonic vibrational frequencies and energies of small NCHC's computed at the MP2 level of perturbation theory (this work). The $OBeH_2$ results are from configuration interaction calculations (Ref. 18) (R is the distance between the metal and the H–H bond midpoint).

	HH_2^+	LiH_2^+	BeH_2^{+2}	$OBeH_2$[18]	H_2
R (Å)	0.753	1.983	1.553	1.531	
r_{H-H} (Å)	0.870	0.745	0.809	0.772	0.736
ω_{H-H} (cm^{-1}	3481	4392	3642	4014	4520
ω (cm^{-1})	2815	497,741	1062,1249		
$E(E_h)$	−1.334867	−8.450237	−14.902950		−1.165836
D_e (Kcal/mol)		6.25	54.87	15.4	
D_o (Kcal/mol)		4.66	52.82		

the complexes is not considerably different from that of the free hydrogen molecule. (The 0.736 Å bond for the free H_2 is lengthened to 0.745 Å for LiH_2^+ and 0.809 Å for the more tightly bound Be H_2^{+2}. The H–H stretching vibrational frequency is 4520 cm^{-1} for H_2, shifted to 4392 cm^{-1} in the Li^+ complex and 3642 cm^{-1} in the Be^{+2} complex. (Compare also with 3481 cm^{-1} for H_3^+.)

In both cases we look at a metal atom where all outer electrons have been removed, and only the $1s^2$ core is occupied; the metals are very electron deficient and therefore bind H_2 in a two-electron three-center bond giving rise to NCHC's. There is, however, a significant difference in the stability of the two complexes: the binding energy for LiH_2^+ is 6.25 kcal/mol (or 4.66 kcal/mol when the v = 0 vibrational levels are compared), whereas that of BeH_2^{+2} is 54.87 kcal/mol (or 52.82 kcal/mol for the $v = 0$ levels). Examination of the MP2 natural orbitals shows that in both cases the $1s^2$ orbital of the metal core is occupied >1.99, and a H_2 σ_g orbital is occupied by about 1.98 electrons. However, in the case of Li this orbital is almost pure H_2 σ_g, whereas in Be there is a very significant involvement of the outermost s orbitals (low exponent basis functions) of the metal atom, as well as from a diffuse p_z orbital. This significant difference, which accounts for the difference in the binding energy of the two complexes, can be attributed to the fact that Be^{+2} can accommodate two electrons in degenerate n = 2 empty orbitals. Furthermore, the energy of these LUMO's on the metal center lie closer to the energy of the occupied σ_g H_2 orbital, thus maximizing interaction. The difference in the stability of the two NCHC's is not only obvious from the binding energy, but also from the fact that Be is significantly closer to the H–H distance midpoint (1.553 Å compared to 1.983 Å for Li).

Another comparison that can lead to interesting conclusions regarding the binding ability of light metal cations in their interaction with the hydrogen molecule is from one of our previous studies[26] comparing Be^{+2} and Mg^{+2}. In this case both cations have outer empty shells capable of accommodating two electrons. However, the binding energy for MgH_2^{+2} is of the order of 20 kcal/mol compared to about 50 kcal/mol for BeH_2^{+2}.[23,24,26] This difference can be attributed to a combination of factors including increased shielding, incompatibility of HOMO-LUMO levels and destructive interference with d orbitals.

As far as the charged NCHC's of the light metal atoms are concerned, we can summarize that Be^{+2} shows an exceptional behavior where the energetics favor a three-center bond with the hydrogen molecule, Mg^{+2} and Li^{+} being less favorable cases but also forming similar NCHC's.

These conclusions can be extended to the investigation for neutral NCHC's involving light metal atoms. Extensive calculations show that for a neutral complex to be stable, the "effective" charge on the metal atom must be significant. Hence electronegative ligands that contain the oxygen or fluorine atoms are good candidates. Good examples are $OBeH_2$,[23,24] F_2MgH_2[27] and dimer,[28] and H_2LiNO_2.[37] Again, we find that the most stable case is that of Be.

IV. PREDICTION OF A NEW NONCLASSICAL HYDROGEN COMPLEX WITH AN UNUSUAL GEOMETRY: THE $Li_4H_2^{2+}$ CLUSTER

Our earlier work has shown (e.g., Ref. 25) that hydrogen complexes may be formed when more than one metal atom act as the dication moiety, i.e., also when there is metal–metal bonding. Accordingly, we decided to check the possibility of a stable Li_4^{2+}–H_2 complex, at the basic geometry of a tetrahedral Li_4^{2+}, which was recently computed to be metastable,[38] existing 18.4 kcal/mol lower than the separated atoms, but 47.3 kcal/mol higher than Li^{3+} + Li^{+}. The barrier

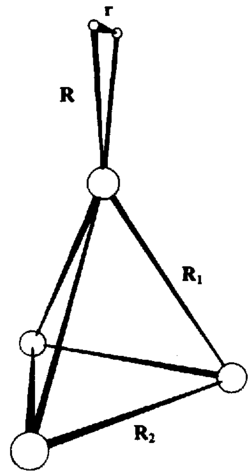


FIGURE 1

to this dissociation is about 3.7 kcal/mol, thereby showing relative stability. The extreme electron deficiency of the Li atoms in this 4c-2e system is one of the features in the binding of many other NCHC's.

Results of the weakly bound NCHC found to exist in the case of Li_4^{2+} and shown in Fig. 1 are given in Table II. The basis set used here is smaller than the ones used in the studies described above,

TABLE II

Structures, harmonic vibrational frequencies and energies of Li_4^{++} and $Li_4H_2^{++}$ (R, R_1, R_2 and r are defined in Fig. 1).

	Li_4^{++}	$Li_4H_2^{++}$	H_2
R (Å)		2.037	
R_1 (Å)	3.443	3.490	
R_2 (Å)	3.443	3.388	
r_{H-H} (Å)		0.744	0.734
ω_{H-H} (cm^{-1})		4412	4556
ω (cm^{-1})	144(3), 162(2), 198	148,149,165,167, 200,479,703	
$E(E_h)$	−29.494934	−30.666734	−1.162636
D_e (Kcal/mol)		5.75	
D_o (Kcal/mol)		4.05	

but a full geometry optimization was performed at the MP2 level of theory, allowing all internal and intermolecular degrees of freedom to vary. Details of the calculations will be given elsewhere.[37] However, it is interesting to note here that small charged Li clusters can be reasonably good candidates for the binding of the hydrogen molecule in a side-on approach. The reported binding energies of Table II are quite significant, and the small lengthening of the H_2 bond by 0.01 Å and shift of the H_2 stretching frequency by about 150 cm^{-1} show a true NCHC. If additional H_2 molecules are added to the corners of the Li_4^{2+} tetrahedron, the system breaks, indicating that there is not enough σ-bond charge-induced polarization and bond electron density capabilities for the larger cluster.

V. CONCLUSION

Not only transition metals with their d electrons,[1–7,15–21] but also light nontransition metals[22–28] as well as nonmetals[8–11] can form complexes where H_2 is bound in molecular form. This unified view of the existence of "nonclassical" hydrogen complexes (NCHC's) suggested in this Comment may provide the impetus for novel experimental attempts toward the synthesis and spectrosocpy of new NCHC's.

As regards theory, the backbone of the understanding of the formation of the NCHC's consists of a combination of notions such as charge polarization, the existence of suitable energy and symmetry matching of HOMO-LUMOs and orbital back-bonding. However, such concepts have only heuristic value. Given the shallowness of the potential energy minima and the fact that some of them are in fact local minima, the prediction of new NCHC's and the ability to interpret quantitatively experimental information on structure and spectra must depend on advanced calculations which include electron correlation (and relativistic effects for heavy atoms).

References

1. G. J. Kubas, Comments Inorg. Chem. 7, 17 (1988): G. J. Kubas, Acc. Chem. Res. **21**, 120 (1988).

2. R. H. Crabtree, Acc. Chem. Res. **23**, 95 (1990).
3. P. Zanello, Comments Inorg. Chem. **11**, 339 (1991).
4. J. K. Burdett, O. Eisenstein and S. A. Jackson, in *Transition Metal Hydrides* ed. A. Dedieu (VCH Verlag, New York, (1991).
5. P. G. Jessop and R. H. Morris, Coord. Chem. Reviews **121**, 155 (1992).
6. D. M. Heinekey and W. J. Oldham Jr., Chem. Rev. **93**, 913 (1993).
7. G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini and H. J. Wasserman, J. Am. Chem. Soc. **106**, 451 (1984).
8. P. R. Schreiner, H. F. Schaefer III and P. vR. Schleyer, J. Chem. Phys. **101**, 7625 (1994) J. D. Watts and R. J. Bartlett, J. Am. Chem. Soc. **117**, 825 (1995).
9. P. R. Schreiner, S. J. Kim, H. F. Schaefer III and P. vR. Schleyer, J. Chem. Phys. **99**, 3716 (1993). G. E. Scuseria, Nature **366**, 512 (1993).
10. (a) C. H. Hu, M. Shen and H. F. Schaefer III, Chem. Phys. Lett. **190**, 543 (1992). (b) P. R. Schreiner, H. F. Schaefer III and P. vR. Schleyer, J. Chem. Phys. **101**, 2141 (1994).
11. T. J. Tague Jr. and L. Andrews, J. Am. Chem. Soc. **116**, 4970 (1994).
12. D. W. Boo and Y. T. Lee, Chem. Phys. Lett. **211**, 358 (1993). For some earlier experimental evidence, see M. D. Sefcik, J. M. S. Henis and P. G. Gaspar, J. Chem. Phys. **61**, 4321 (1974).
13. Y. Cao, J.-H. Choi, B.-M. Haas, M. S. Johnson and M. Okumura, J. Phys. Chem. **97**, 5215 (1993).
14. J. E. Bushnell, P. R. Kemper and M. T. Bowers, J. Phys. Chem. **98**, 2044 (1994).
15. P. J. Hay, Chem. Phys. Lett. **103**, 466 (1984); P. J. Hay, J. Am. Chem. Soc. **109**, 705 (1987).
16. J. Y. Saillard and R. Hoffmann, J. Am. Chem. Soc. **106**, 2006 (1984).
17. H. Babaâ, J. Y. Saillard and R. Hoffmann, J. Am. Chem. Soc. **108**, 4327 (1986).
18. Y. Jean, O. Eisenstein, F. Volatron, B. Maouche and F. Sefta, J. Am. Chem. Soc. **108**, 6587 (1986).
19. J. K. Burdett, J. R. Phillips, M. R. Pourian, M. Poliakoff, J. J. Turner and R. Upmacis, Inorg. Chem. **26**, 3054 (1987).
20. M. Blomberg, U. Brandemark, L. Petterson and P. Siegbahn, Int. J. Qu. Chem. **23** 855 (1983).
21. U. B. Brandemark, M. R. A. Blomberg, L. G. M. Petterson and P. E. M. Siegbahn, J. Phys. Chem. **88**, 4617 (1984).
22. P. Valtazanos and C. A. Nicolaides, Chem. Phys. Lett. **172**, 254 (1990).
23. C. A. Nicolaides and P. Valtazanos, Chem. Phys. Lett. **174**, 489 (1990).
24. C. A. Nicolaides and P. Valtazanos, Chem. Phys. Lett. **176**, 239 (1991).
25. C. A. Nicolaides and P. Valtazanos, in *Theoretical and Computational Models for Organic Chemistry*, eds. S. J. Formosinho, I. G. Csizmadia and L. G. Arnant (Kluwer, Dordrecht, 1991), p. 355.
26. E. D. Simandiras and C. A. Nicolaides, Chem. Phys. Lett. **185**, 529 (1991).
27. C. A. Nicolaides and E. D. Simandiras, Chem. Phys. Lett. **196**, 213 (1992).
28. E. D. Simandiras and C. A. Nicolaides, Chem. Phys. Lett. **223**, 233 (1994).
29. C. A. Nicolaides, Chem. Phys. Lett. **161**, 547 (1989).
30. C. A. Nicolaides, M. Chrysos and P. Valtazanos, J. Phys. B **23**, 791 (1990).
31. H. Basch, S. Hoz and M. Goldberg, Israel J. Chem. **33**, 403 (1993).
32. P. Valtazanos and C. A. Nicolaides, J. Chem. Phys. **98**, 549 (1993).
33. M. E. Schwartz and L. J. Schaad, J. Chem. Phys. **47**, 5325 (1967).
34. C. W. Bauschlicher, S. V. O'Neil, R. K. Preston and H. F. Schaefer, J. Chem. Phys. **59**, 1286 (1973).
35. C. Moller and M. S. Plesset, Phys. Rev. **46**, 618 (1934), as implemented for

the energy, gradients and second derivatives of the energy in CADPAC5. The Cambridge Analytic Derivatives Package, Issue 5, Cambridge 1992, a suite of quantum chemistry programs developed by R. D. Amos with contributions from I. L. Alberts, J. S. Andrews, S. M. Colwell, N. C. Handy, D. Jayatilaka, P. J. Knowles, R. Kobayashi, N. Koga, K. E. Laidig, P. E. Maslen, C. W. Murray, J. E. Rice, J. Sanz, E. D. Simandiras, A. J. Stone and M.-D. Su.

36. For Li and Be atoms we use 14s8p7d4f/9s8p7d3f and 14s7p7d4f/9s7p7d3f basis sets, respectively, based on C. W. Bauschlicher, S. R. Langhoff and H. Partridge, J. Chem. Phys. **84**, 901 (1986), with extensions for extra diffuse and tight functions. For the Li atom in the cluster complex the basis is reduced to 8s5p2d contracted functions. For H we use a 10s4p1d/6s4p1d basis for the triatomic calculations and a 3s2p set for the cluster complex.
37. E. D. Simandiras and C. A. Nicolaides, to be published.
38. M. N. Glukhovtsev, P. vR. Schleyer and A. Stein, J. Phys. Chem. **97**, 5541 (1993).