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REGULAR ARTICLE

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Intermolecular dihydrogen bonding in VI, VII, and VIII group octahedral metal hydride complexes with water

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Abstract. The nature of dihydrogen bonding (DHB) in VI, VII, and VIII group octahedral metal hydride complexes with H_2O has been studied systematically using quantum theory of atoms-in-molecule (QTAIM) analysis. A dihydrogen bond (H$\cdots$H) between hydride ligand and hydrogen of H_2O is revealed in QTAIM analysis with the identification of a bond critical point (bcp). The DHB is due to the donation of electron density from the hydride ligand to the hydrogen of H_2O. A strong linear correlation is observed between intermolecular H$\cdots$H distance (d_{HH}) and electron density (ρ) at the bcp. Structural parameters suggested the highly directional nature of DHB. Weak secondary interactions between oxygen of water and other ligands contribute significantly to the binding energy (E_{int}) of DHB complex (2.5 to 13.2 kcal/mol). Analysis of QTAIM parameters such as kinetic- (G_c), potential- (V_c) and total electron energy density (H_c) revealed the partially covalent character of DHB in majority of the complexes while a few of them showed closed shell character typical of purely non-covalent interactions.

Keywords. Dihydrogen bond; QTAIM; metal hydrides; non-covalent interaction.

1. Introduction

The term “dihydrogen bond” (DHB) was first proposed by Crabtree *et al.*, in 1996 when they investigated certain N–H$\cdots$H–B intermolecular interactions.[1] They also explored the existence of similar M–H$\cdots$H–C (M, transition metals) type of unconventional hydrogen bonding and reported the internuclear H$\cdots$H distance, d_{HH} in the range 1.6–2.1 Å.[2] The experimental studies disclosed that the stabilizing energy of DHB is within 3–7 kcal/mol[3,4] while considerable number of experimental and theoretical studies report on the characterization of DHB systems.[5–9] Various groups have studied the distinctive features of DHB systems using spectroscopy, proton affinity measurements, and analysis of thermodynamic data.[10–14] Today, DHB has been enrolled as a pretty well-understood concept in chemical bonding whereas potential new applications of DHB is getting unfolded in many emerging areas such as hydrogen storage, water-splitting reactions, crystal engineering, catalyst tailoring and catalysis.[15–17] The $D–H^{\delta+}\cdots{}^{\delta+}H–A$ interaction, (where D and A are proton donors and acceptors, respectively) plays a crucial role in proton transfer processes and σ bond metathesis reactions.[18,19] Szymczak *et al.*, reported in detail the complexation patterns of $(\eta^2-H_2)/D\cdots(H_2)^+\cdots A^-$ ion pairs and the related dihydrogen elimination reactions.[20] Belkova *et al.*, explored the equilibrium between dihydrogen bond intermediate and associated ion paired dihydrogen complex formation in a system CpRu(dppe)H (dppe = $Ph_2PCH_2CH_2PPh_2$) with HA.[10] Later studies in this area showed the DHB formation between two metal hydrides, as for example, $[OsH_2(PMePh_2)_4]$/$[CpM(H)(CO)_3]$ and $[(^{tBu}PCP)Ni(H)]/[CpW(H)(CO)_3]$ (^{tBu}PCP = 2,6-$C_6H_3(CH_2P^{tBu}{}_2)_2$).[21] Formation of intramolecular DHB has been well established in various other complex systems, such as, $[IrH_2(PMe_3)(2\text{-}NH_2C_6H_4)(PPh_3)_2]^{0/+1}$, $[Ir(PEt_2Ph)_2H_2(PPh_3)_2(2\text{-}NH_2C_5H_4$

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Table 1. Structural parameters, QTAIM parameters and binding energy (E_{int}) for dihydrogen complex. dpp = 1,2-diphosphine-propane, pae = 2-phospino-1-amine ethane, dpe = 1,2-diphosphine-ethane, dpcp = 1,2-diphosphine-cyclopentane, en = ethylene diamine, imd = imidazole, dpm = 1,2-diphosphine methane, dpe = 1,2 diphosphine ethane, py = 1-pyrrole.

Sl. No.	Complex interacting with H_2O	d_{HH} Å	ρ au	$\nabla^2\rho$ au	V_c au	G_c au	$-G_c/V_c$ au	E_{int} kcal/mol	$E_{int(sol)}$ kcal/mol
1.	$Mn(CO)_4(PH_3)H$	2.048	0.011	0.035	−0.006	0.007	1.218	5.7	2.8
2.	$Mn(CO)_3(PH_3)_2H$	1.669	0.024	0.046	−0.015	0.013	0.886	6.4	3.1
3.	$Mn(CO)_2(PH_3)_3H$	1.648	0.026	0.046	−0.016	0.014	0.869	6.6	3.6
4.	$Mn(CO)(PH_3)_4H$	1.642	0.027	0.046	−0.016	0.014	0.86	6.7	3.9
5.	$Mn(PH_3)_5H$	1.641	0.026	0.045	−0.016	0.014	0.864	6.9	4.0
6.	$Mn(CO)_3(dpp)H$	1.669	0.024	0.044	−0.014	0.013	0.889	8.0	3.1
7.	$Mn(dpe)_2N_2H$	1.624	0.026	0.044	−0.015	0.013	0.857	7.1	4.1
8.	$Mn(CO)(dpe)_2H$	1.630	0.026	0.044	−0.015	0.013	0.861	7.4	4.2
9.	$Mn(PH_3)_4N_2H$	1.634	0.027	0.046	−0.016	0.014	0.859	6.6	3.6
10.	$Fe(dpe)_2(CN)H$	1.636	0.027	0.046	−0.016	0.014	0.867	9.0	4.4
11.	$Fe(CO)_2(PH_3)_2ClH$	1.971	0.014	0.038	−0.008	0.009	1.112	5.7	3.2
12.	$Fe(CO)_2(PH_3)_2FH$	2.056	0.012	0.034	−0.007	0.008	1.156	5.6	3.3
13.	$Fe(dpe)_2(Py)H$	1.626	0.027	0.046	−0.016	0.014	0.863	6.9	4.3
14.	$Fe(dpe)_2(Cl)H$	1.643	0.026	0.046	−0.015	0.014	0.873	9.0	4.4
15.	$Re(CO)_3(PH_3)_2H$	1.701	0.024	0.045	−0.014	0.013	0.898	7.6	3.2
16.	$Re(CO)_2(PH_3)_3H$	1.689	0.024	0.044	−0.014	0.013	0.887	7.3	3.3
17.	$Re(N_2)(PH_3)_4H$	1.685	0.024	0.045	−0.014	0.013	0.892	6.8	3.2
18.	$Re(CO)(PH_3)_4H$	1.685	0.025	0.044	−0.014	0.013	0.884	7.0	3.4
19.	$Ru(PH_3)_4(SiH_3)H$	1.727	0.022	0.043	−0.013	0.012	0.912	6.5	3.3
20.	$Ru(PH_3)_3Cl(CO)H$	2.006	0.013	0.035	−0.007	0.008	1.125	5.5	2.8
21.	$Ru(PH_3)_2(CO)_2(NCO)H$	2.062	0.011	0.033	−0.006	0.007	1.177	5.6	2.8
22.	$Ru(PH_3)_3F(CO)H$	1.811	0.018	0.042	−0.011	0.011	0.985	5.3	2.9
23.	$Ru(dpe)_2ClH$	1.718	0.022	0.043	−0.013	0.012	0.912	8.5	3.9
24.	$Ru(PH_3)(SiH_3)(CO)_3H$	2.052	0.011	0.033	−0.006	0.007	1.17	5.3	2.4
25.	$Ru(PH_3)_2COCl(imd)H$	1.987	0.014	0.035	−0.007	0.008	1.09	6.3	3.2
26.	$Ru(dpm)_2ClH$	1.72	0.022	0.042	−0.013	0.012	0.911	7.7	3.4
27.	$Ru(pae)_2ClH$	1.645	0.028	0.046	−0.016	0.014	0.852	13.2	6.1
28.	$Ru(en)(PH_3)_2ClH$	1.72	0.023	0.043	−0.013	0.012	0.905	10.6	5.1
29.	$Mo(CO)_3(PH_3)(NO)H$	1.793	0.02	0.041	−0.011	0.011	0.962	6.6	3.4
30.	$Mo(PH_3)_3(CO)(NO)H$	1.669	0.021	0.042	−0.012	0.011	0.934	7.8	3.8
31.	$Mo(PH_3)_4(NO)H$	1.665	0.026	0.043	−0.015	0.013	0.855	7.4	3.6
32.	$Mo(NO)(dpcp)_2H$	1.623	0.027	0.043	−0.016	0.013	0.834	8.5	4.1
33.	$Mo(dpe)_2(NO)H$	1.627	0.027	0.042	−0.016	0.013	0.834	8.6	4.2
34.	$Mo(dpe)(CO)_2(NO)H$	1.661	0.025	0.042	−0.014	0.012	0.863	8.6	3.0
35.	$W(CO)_2(PH_3)_2(NO)H$	1.815	0.02	0.044	−0.011	0.011	0.991	6.8	3.3

Table 1. (*contd.*)

Sl. No.	Complex interacting with H_2O	d_{HH} Å	ρ au	$\nabla^2\rho$ au	V_c au	G_c au	$-G_c/V_c$ au	E_{int} kcal/mol	$E_{int(sol)}$ kcal/mol
36.	$W(CO)(PH_3)_3(NO)H$	1.682	0.027	0.048	−0.015	0.013	0.886	7.9	3.4
37.	$W(PH_3)_4(NO)H$	1.681	0.027	0.046	−0.014	0.013	0.882	7.5	3.6
38.	$W(dpe)_2(NO)H$	1.64	0.027	0.045	−0.015	0.013	0.855	8.7	4.1
39.	$W(CH)(dpe)_2H$	1.63	0.028	0.044	−0.016	0.013	0.837	9.3	4.4
40.	$W(CO)_3(PH_3)(NO)H$	1.863	0.018	0.043	−0.01	0.01	1.03	6.8	3.1

N)]$^+$, $[IrH_3(PPh_3)_2(2\text{-}NH_2C_5H_4N)]$, $[Ir(PMe_3)_4(H)(OH)]$ and $[Fe(H)_2(H_2)(PEt_2Ph)_4]$.[2]

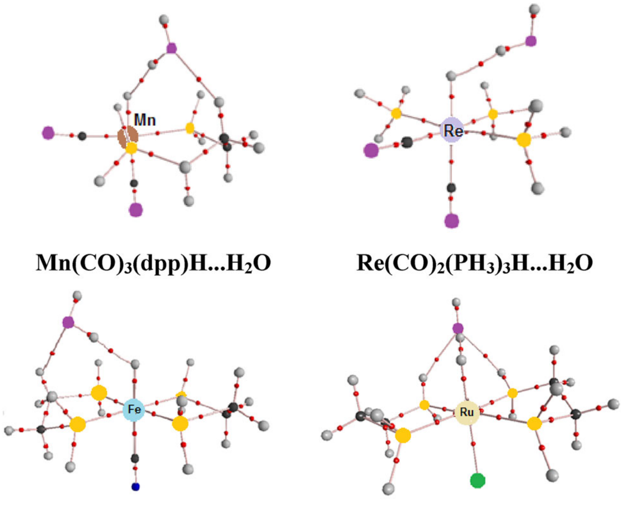
In our previous study, the formation of Ru–H···H–O type DHB complex is invoked to explain the mechanism of water splitting ability of Milstein catalyst[22] and several other studies showed that increasing the hydricity of M–H bond is attractive for designing water splitting reactions of metal hydride complexes.[17–20] In a recent study, we showed that hydricity of several group VI and group VII octahedral metal hydride complexes of Mo, W, Mn, and Re complexes can be quantified from the electrostatic potential minimum observed on the hydride ligand.[23] These studies suggest that the M–H···H–O DHB interaction and the associated H_2 elimination reaction is intimately connected with the nature of H···H bond. Grabowski *et al.*, and Alkorta *et al.,* have used quantum theory of atoms-in-molecule (QTAIM) analysis on the topographical properties of electron density at the H···H contact of small linear molecules to describe the nature of interaction as well as to find a correlation between energetic parameters and d_{HH}.[7,24,25] The nature of DHB was also studied by linear attack of small inorganic/organic molecules (NH_3, CH_4, HF, *etc.*) and metal hydrides such as SiH_4, LiH, BeH_2, MgH_2, *etc.*[26–28] In the present work, QTAIM analysis is used to predict the nature of dihydrogen bonding in transition metal complexes. Further, by studying M–H···H–O interaction, suitable hydride complexes can be proposed for efficient water-splitting reactions.

2. Computational methodology

The quantitative structural and bonding information was obtained from the topological QTAIM analysis proposed by Bader.[29,30] The molecules were scrutinized in terms of critical points (at the critical points $\nabla\rho = 0$). Four types of critical points were found in electron density topography, *viz.*, (3, −3) maxima, (3, +3) minima, (3, +1) saddle point and (3, −1) saddle point. The maxima correspond to nuclear positions and a minimum appears in caged structures. Ring-shaped molecules show (3, +1) saddle point while (3, −1) saddle points were seen between bonded pairs of atoms. The (3, −1) critical points are also called bond critical point (bcp). Laplacian of electron density at bcp, $\nabla^2\rho$, is another criteria for assessing the nature of the bond, which relate with kinetic (V_c) and potential (G_c) energy densities at the bcp through the local virial theorem (1),

$$(1/4)\nabla^2\rho = 2G_c + V_c \tag{1}$$

by which partially covalent as well as closed shell interaction can be resolved from the sign of the sum of V_c and G_c. The summation ($V_c + G_c$) is called the total electron energy density, H_c where a positive value represents weak



$Mn(CO)_3(dpp)H...H_2O$ **$Re(CO)_2(PH_3)_3H...H_2O$**

$Fe(dpe)_2(CN)H...H_2O$ **$Ru(pae)_2ClH...H_2O$**

Figure 1. Dihydrogen bond interaction and secondary interaction of some representative complexes with water are shown by QTAIM molecular graph. Atom colours: ash = H, black = C, purple = O, blue = N, green = Cl, orange = P and small red sphere = bcp.

or closed shell bonding and a negative value means partially covalent bond.[30] Wave functions (wfn) of optimized geometry are required to estimate QTAIM parameters. All calculations were performed at B3LYP[31,32] density functional theory as implemented in the Gaussian03 program.[33] Effective core potential (ECP) of Hay and Wadt with an added f polarization functions were used for transition metals to replace the core electrons.[34] Double-ξ valence basis set (LANL2DZ) was selected for transition metals and for all other atoms 6-31G(d, p) basis set was chosen.[34,35] Single point calculations at the same level were performed for describing solvation effect using SMD method.[36] To reduce computation time, various bulky phosphine ligands of complexes were replaced with simple phosphine ligand (PH_3).

3. Results and Discussion

We have modelled Mo, W, Mn, Re, Fe and Ru metal hydride complexes comprising of various ligands in the coordination sphere. Theoretical observations of structural parameters for most of the complexes were explained in our previous paper.[37] Majority of the complexes contain phosphine ligands which enhance the negative charge on the hydride ligand. Other ligands in the complexes are $H_2PCH_2CH_2PH_2$, $H_2NCH_2CH_2NH_2$, heterocyclic ligand, phosphine, silyl, chloro, fluoro, C≡CH, NO, N_2, and CNO. All structural formulas can be seen in Table 1. The study focuses on DHB formation between the hydride ligand in the complex and hydrogen of water.

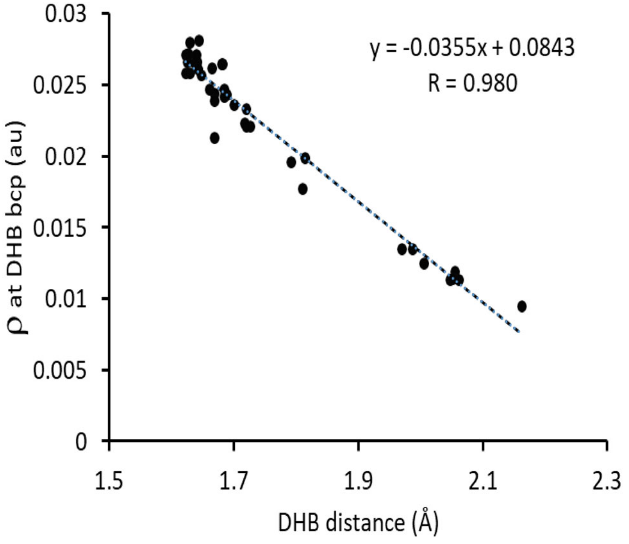


Figure 2. Correlation between ρ at DHB bcp and d_{HH}.

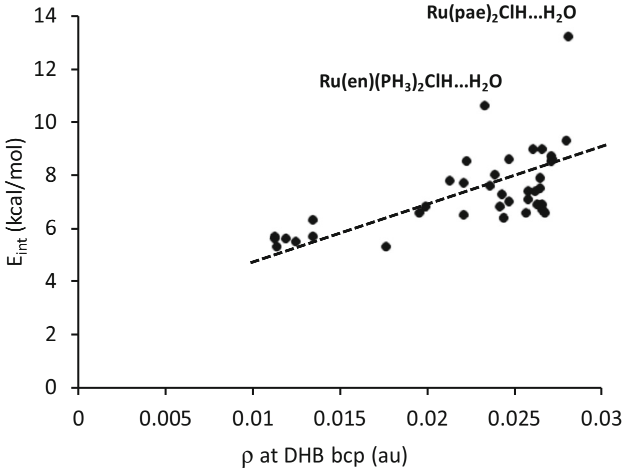
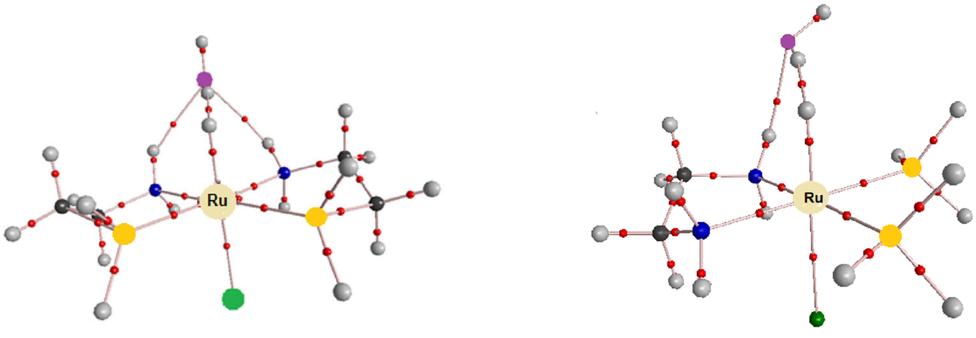
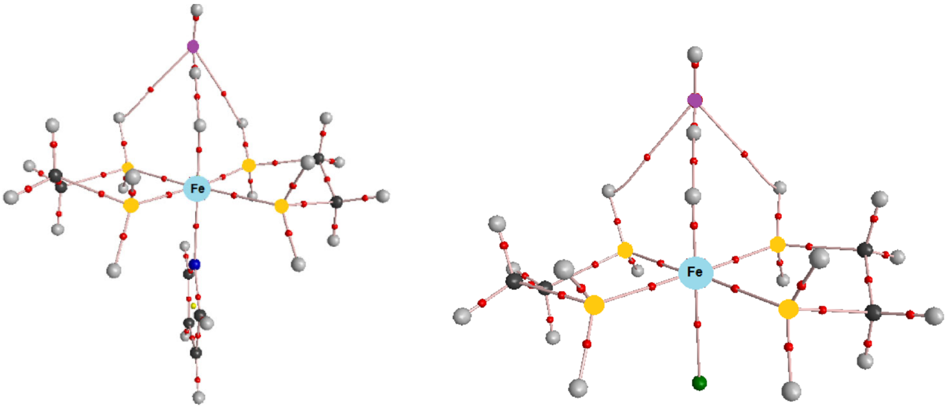


Figure 3. Correlation between ρ at DHB bcp and binding energy. The two Ru complexes are not used in the linear plot.

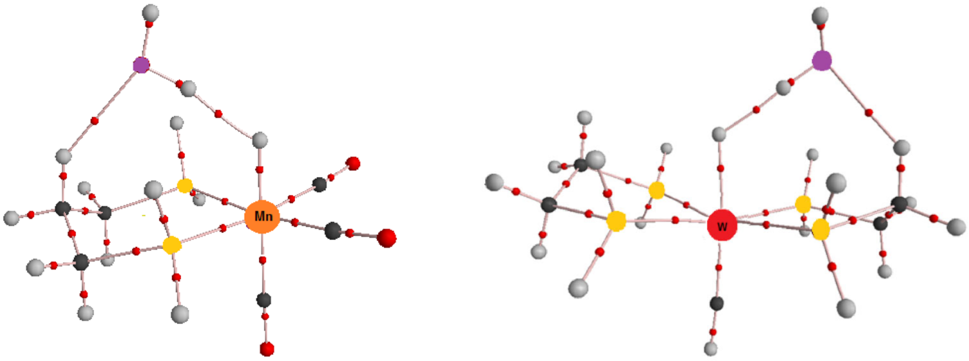
The d_{HH} of all complexes lies in the range 1.623 Å–2.062 Å (Table 1). This range is consistent with the distance reported for the organic and linear s or p block hydride systems as well as for many transition metal complexes.[38–40] $Mn(CO)_4(PH_3)H\cdots H_2O$, $Re(CO)_5H\cdots H_2O$, $Ru(PH_3)_3Cl(CO)H\cdots H_2O$, $Ru(PH_3)_2(CO)_2(NCO)H\cdots H_2O$ and $Ru(PH_3)_2(CO)_3H\cdots H_2O$ complexes show higher d_{HH} values compared to other complexes. The binding energy (E_{int}) for the water adducts are in the range of 5.3 to 13.2 kcal/mol, which is similar to intramolecular H···H bond strength reported by Crabtree *et al.*[3,41] The highest E_{int} 10.6 kcal/mol and 13.2 kcal/mol are observed for the Ru complexes $Ru(en)(PH_3)_2ClH$ and $Ru(pae)_2ClH$, respectively, whereas the weakest E_{int} 5.3 kcal/mol is observed for $Ru(PH_3)_3F(CO)H\cdots H_2O$. Lower ranges of E_{int} correlate to larger d_{HH} values. The binding energy of water



$Ru(pae)_2ClH...H_2O$ $Ru(en)(PH_3)_2ClH\ldots H_2O$



$Fe(dpe)_2(Py)H...H_2O$ $Fe(dpe)_2(Cl)H...H_2O$



$Mn(CO)_3(dpp)H...H_2O$ $W(CH)(dpe)_2H\ldots H_2O$

Figure 4. QTAIM molecular graph of representative DHB complexes showing secondary interactions.

adducts is also calculated with the inclusion of solvent effect ($E_{int(sol)}$). Solvation effects decreased E_{int} by 50–60% compared to the gas phase values (Table 1).

Molecular graph as seen in QTAIM is provided in Figure 1 for some representative cases. A bcp is observed for the H$\cdots$H DHB interaction in all the complexes. The ρ value at bcp for all the systems is in the range 0.011–0.028 a.u. The strength of DHB is proportional to ρ and it decreases with increase in d_{HH} distance (Figure 2). The Laplacian $\nabla^2\rho$ of all the systems fall in this range 0.033–0.048 a.u. which is similar to the range reported by Grabowski *et al.*, (0.049–0.016 a.u.) for a wide spectrum of dihydrogen interactions.[42]

The M–H$\cdots$HO type DHB formation leads to a slight elongation (0.005 Å–0.020 Å) of OH bond distance of water (d_{OH}). Further, the H$\cdots$HO angle (θ) is in the range 141–179° suggesting that among various possible orientations of water around the hydride ligand, a collinear approach of M–H and OH bonds is mostly preferred, indicating the highly directional nature of DHB.

An increasing trend in binding energy (E_{int}) with an increase in the ρ value at the DHB bcp is observed for most of the complexes (Figure 3) indicating that the water adduct formation depends on the strength of DHB energy. The deviations in the linear trend can be attributed to interactions other than DHB (secondary interactions). For instance, a noticeable deviation in the plot shown by Ru(pae)$_2$ClH$\cdots$H$_2$O can be attributed to the two NH$\cdots$OH, interactions as seen in the QTAIM molecular graph (Figure 4) between the oxygen of water and the NH bonds of the chelating ligands. Such interactions lead to significant rise in binding energy (13.2 kcal/mol). The complexes, Fe(dpe)$_2$(PY)H$\cdots$H$_2$O and Fe(dpe)$_2$(Cl)H$\cdots$H$_2$O also exhibit a similar kind of interaction between the PH bonds of the chelating ligand and oxygen of water. Similarly, the higher binding energy of Ru(en)(PH$_3$)$_2$ClH$\cdots$H$_2$O can be attributed to the presence of one NH$\cdots$OH, interaction (Figure 4). A secondary interaction between a CH$_2$ unit of a chelating ligand and oxygen of water is also possible. However, such interactions are very weak and do not significantly alter the correlation trend. Examples belonging to this class of complexes are Mn(CO)$_3$(dpp)H$\cdots$H$_2$O, Mn(dpe)$_2$N$_2$H$\cdots$H$_2$O, Fe(dpe)$_2$(CN)H$\cdots$H$_2$O, Ru(dpe)ClH$\cdots$H$_2$O, Ru(dpm)$_2$ClH$\cdots$H$_2$O and Mo(dpe)$_2$(NO)H$\cdots$H$_2$O.

The positive $\nabla^2\rho$ values observed for all the dihydrogen complexes suggest their weak non-covalent nature and such interactions lead to the contraction of electron density towards each hydrogen nucleus. In all the cases, $|V_c| > 2G_c$ indicating that the interactions are non-covalent.[30] According to Ziółkowski *et al.,* a bcp showing a purely non-covalent interaction has the ratio $-G_c/V_c$ greater than one.[43] Figure 5 gives a linear relationship between DHB bond distance and $-G_c/V_c$ which indicates that only eight out of forty complexes studied herein fulfil this criterion. The purely covalent to partially covalent complexes can also be distinguished well from the sign of H_c (Table 1). Positive H_c values in the range 0.000 to 0.0013 au correspond to purely non-covalent closed shell interaction while the rest in the range −0.0001 and −0.0027 a.u. can be attributed to the partially covalent interaction.[42,44] The DHB complexes with d_{HH} in the range of 1.863–2.062 Å belong to purely non-covalent and those in the range 1.623–1.815 Å belong to partially covalent complexes (Figure 5). The partially covalent nature of the DHB is conducive for H$_2$ elimination reactions.[45,46]

4. Conclusions

The nature of dihydrogen bonding in octahedral metal hydride complexes (metal = Mn, Re, Mo, W, Fe and Ru) with H$_2$O has been studied using QTAIM analysis.

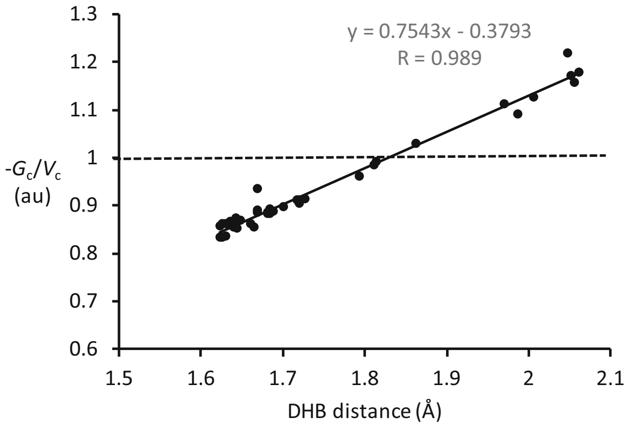


Figure 5. Correlation between QTAIM parameters and d_{HH}.

A bcp between H$\cdots$H bond indicates a weak dihydrogen bond (DHB) formation between the hydrogen of water and the hydride of the metal complex. Partially covalent nature of DHB is revealed for the majority of the complexes while a few of them showed closed shell and purely non-covalent interactions. The highly directional nature of DHB is revealed through structural analysis while the energetics showed stabilizing secondary interactions between the oxygen of water and nearby ligands. The partially covalent character of DHB is helpful for promoting H$_2$ elimination reaction from the complexes.

Supporting Information (SI)

Tables showing secondary interaction data, and coordinates of all complexes are given in supplementary information available at www.ias.ac.in/chemsci.

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