

Computational Design of Functional and Structural Mimics of the Active Site of [FeFe]-Hydrogenase

Final Technical Report

CSIR Scheme No: 01(2912)/17/EMR-II



Submitted by

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FORM-F



COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
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PROFORMA FOR PREPARING FINAL TECHNICAL REPORT

(Five copies of the report must be submitted immediately after completion of the research scheme)

1. Title of the scheme

Computational Design of Functional and Structural Mimics of the Active Site of [FeFe]-Hydrogenase	Scheme No.: 01(2912)/17/EMR-II dated 03-05-2017 Date of Commencement : 01/06/2017 Date of termination : 31/05/2020
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2. Name and address of Principal Investigator

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3. Name of Sponsoring laboratory of CSIR (If applicable)

Not applicable

4. Total grant sanctioned and expenditure during the entire tenure

	Amount Sanctioned	Expenditure
Staff	Nil	Nil
Contingency	Rs. 1,40,714.00	Rs. 86,480.00
Equipment	Rs. 3,00,000.00	Nil (The whole amount was returned to CSIR vide Demand Draft No. 569666 dated March 27, 2019)
Total	Rs. 4,40,714.00	Rs. 86,480.00

5. Equipment(s) purchased out of CSIR grant

Name	Cost
Not Applicable	

6. Research fellows associated with scheme

Name& Designation	Date of Joining	Date of leaving
Not applicable		

7. Name(s) of the fellow(s) who received Ph.D. by working in the scheme, along with the Title(s) of thesis: **Not applicable**

8. List of research papers published:

(i) B. Borthakur, A. Vargas and A. K. Phukan. A Computational Study of Carbene Ligand Stabilization of Biomimetic Models of the Rotated H_{red} State of [FeFe]-Hydrogenase. *Eur. J. Inorg. Chem.* **2019**, 2295–2303.

(ii) B. Borthakur and A. K. Phukan, Can carbene decorated [FeFe]-hydrogenase model complexes catalytically produce dihydrogen? An insight from theory. *Dalton Trans.* **2019**, 48, 11298-11307.

9. Details of new apparatus or equipment designed or constructed during the investigation:

Not applicable

10. The likely impact of the completed work on the scientific/technological potential in the country :

See **Enclosure-I**

11. Is the research work done of some industrial or agricultural importance and whether patent(s) should be taken? Yes/No; if yes, what action has been/should be taken: **No**

12. How has the research work complemented the work of CSIR Laboratory that sponsored your scheme? **Not applicable**

13. Detailed account of the work carried out in terms of the objective(s) of the project and how far they have been achieved; results and discussion should be presented in the manner of a scientific paper/project report in about 5000 words; and this should be submitted as Enclosure-II to this report.

See **Enclosure-II.**

14. An abstract of research achievements in about 200-500 words, suitable for publication.

The work was divided into two parts. In the first part, we performed studies toward stabilization of the fully rotated conformation at one of the iron center for the reduced Fe(I)Fe(I) state in chelated cyclic alkyl amino carbene (CAAC) substituted biomimetic hydrogenase model complex. This study indicates that the spatial orientation of the chelated NHCs at one of the iron center plays a major role in determining the geometry at the other iron center. We also made an attempt at explaining the electronic origin behind the favorability of rotated vs unrotated structure in asymmetrically substituted chelated vs monodentate NHC complexes.

In the second part, we studied the possibility of carbene decorated [FeFe]-hydrogenase model complexes in the catalytic production of dihydrogen. Cyclic alkyl amino carbene (CAAC) anchored [FeFe]-hydrogenase model complex featuring rotated conformations at one of the iron centers are found to be promising candidate for effective production of dihydrogen. A stepwise comparison of the complete mechanism using the CAAC stabilized model complex has been performed with that of an experimentally isolated one. Interestingly, the reduction events involved in the catalytic cycles are found to be more favorable than those previously reported for a similar experimentally known system. Furthermore, the computed ΔpK_a values indicate that the distal iron center with a vacant coordination site is more basic compared to the amino nitrogen atom of the azadithiolate bridge. We also made an attempt to determine the oxidation states of the iron centers for the intermediates involved in the catalytic cycles on the basis of the computed Mössbauer isomer shift and Mulliken spin density values.

15. Mention here whether or not the unspent grant has been refunded to CSIR:

The unspent grant has been refunded to CSIR vide Demand Draft (DD) Nos. 535350 and 535178

(DD No. 535350 dated 04.10.2021 for an amount of Rs. 54,234/- & DD No. 535178 dated 16.06.2021 for an amount of Rs. 3,303).

Date: 07/12/2021



Signature of PI

Note: Final Technical Report is expected to be self-contained complete report of the work done.
Please do not leave any column unanswered.

Likely impact of the completed work on the scientific/technological potential in the country

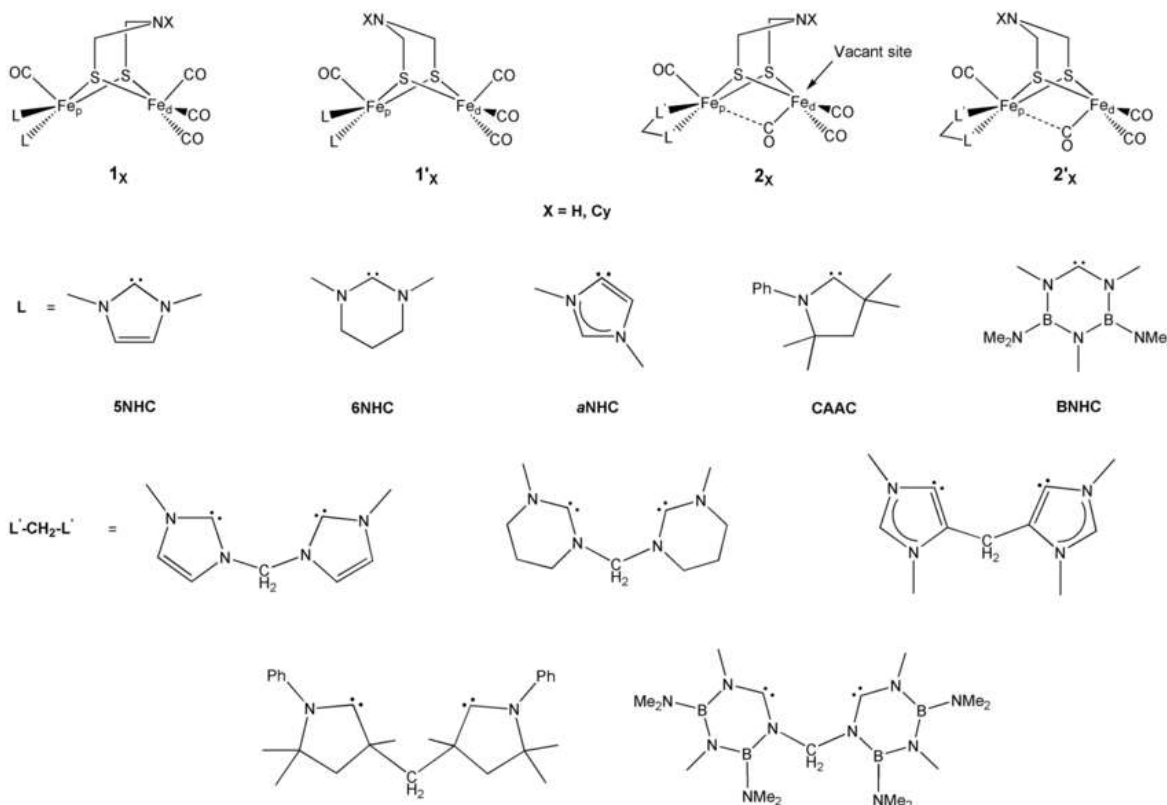
We hope that the insight obtained from our computational study will inspire synthetic chemists towards dihydrogen production, employing carbene anchored biomimetic [FeFe]-hydrogenase model complexes.

Detailed account of the work carried out in terms of the objective(s) of the project

The project aimed to fulfill the following three objectives –

- (1) To design [FeFe] – H₂ase model complexes by installation of a variety of NHCs at the iron centers.
- (2) To study the structural and electronic features of model complexes which mimic the key characteristics (e.g., presence of inverted pyramidal geometry at one of the iron center) of the [FeFe] – H₂ase active site in both the reduced as well as in the oxidized states.
- (3) To study the complete catalytic cycle of the formation of dihydrogen using the NHC substituted model complexes.

To address the first two objectives, we have considered a variety of structurally and electronically different *N*-heterocyclic carbenes (NHCs) as substituents for one of the iron center in the reduced Fe(I)Fe(I) state of [FeFe]-hydrogenase model complexes. The model complexes studied were unsymmetrically substituted by both monodentate and chelated NHCs (Scheme 3).



Scheme 3: Schematic representation of the NHC substituted model complexes (X= H/Cyclohexyl)

In all of these complexes, we have considered only the basal/basal isomer with respect to NHC coordination at Fe as X-ray diffraction study confirms that the bis-carbene ligand is in a basal/basal environment in similar experimentally known complexes. The carbene substituted Fe center is referred as proximal (Fe_p) whereas the other one as distal (Fe_d) (Scheme 1). The optimized structures of some representative molecules are given in Figure 1.

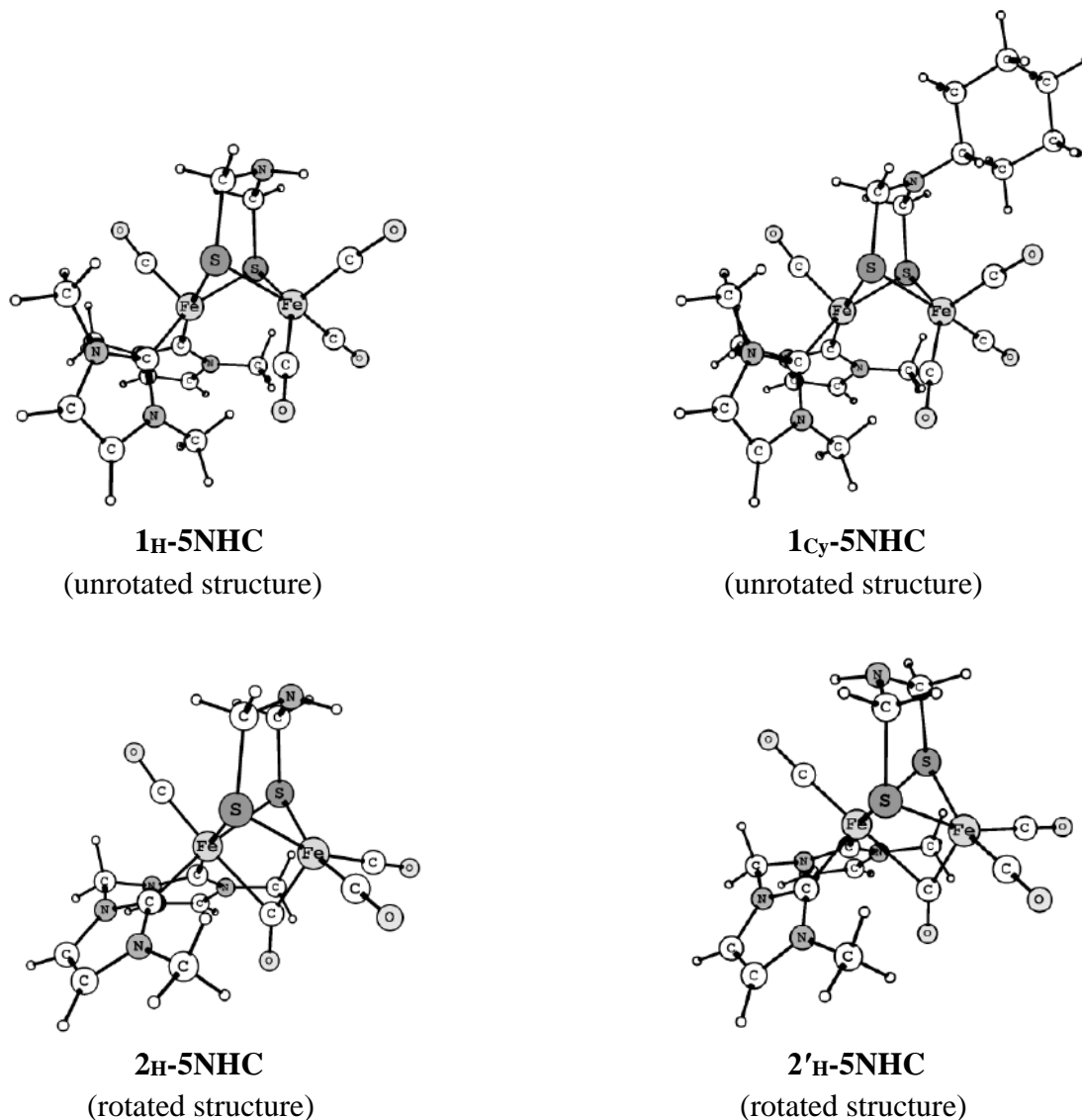


Figure. 1: Optimized geometry of complexes with monodentate (top) and chelated (bottom) 5NHC ligands.

It should be noted that the use of monodentate five-membered NHCs (5NHCs) did not result in rotated structures using either hydrogen or cyclohexyl groups as the azadithiolate bridgehead. However, complete rotation of the $\text{Fe}_d(\text{CO})_3$ unit is observed for the model complexes with chelated 5NHCs (**2_x-5NHC**, Scheme 3) resulting in an inverted square pyramidal geometry at Fe_d with a semi-bridging carbonyl group between the two iron centers (Figure 1) implying that

chelation of the NHC ligands plays a crucial role for the stabilization of the rotated structure in the Fe(I)Fe(I) state. Similar results were obtained in case of previous experimental studies for related phosphine complexes. Accordingly, we have considered only the chelated versions of the remaining four different types of NHCs as substituents at the proximal iron center. It was observed that the chelated complexes have substantially shorter Fe_p-Fe_d bond lengths (2.595-2.605 Å) compared to those with monodentate ones (i.e., **1_X**-5NHC and **1'_X**-5NHC, 2.715-2.741 Å). Chelation results in not only symmetric coordination of the NHC ligands with equal Fe_p-C_c (C_c=carbene carbon) bond lengths but also greater degree of stabilization of the Fe_p-Fe_d bonding interaction in the rotated geometry. An MO analysis for both **1_H**-5NHC and **2_H**-5NHC (Figure 2) shows that in **1_H**-5NHC, the MO representing the Fe_p-Fe_d bonding interaction is HOMO-1 (-4.1 eV) while in **2_H**-5NHC, the same turned out to be significantly stable and becomes HOMO-8 (-5.6 eV).

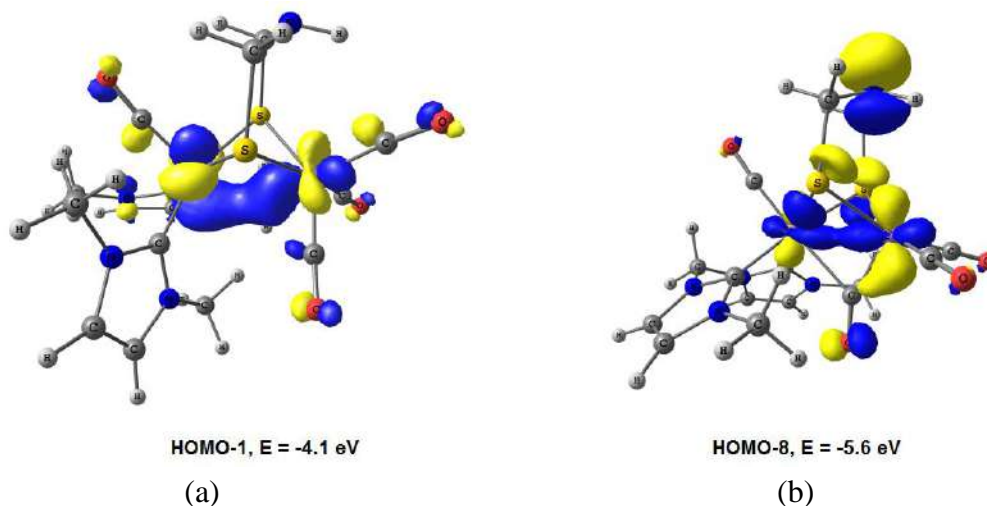


Figure 2: Molecular orbital representing the Fe_p-Fe_d bonding interaction in (a) **1_H**-5NHC and (b) **2_H**-5NHC.

Interestingly, installation of all the remaining four types of chelated NHCs at the proximal iron center also results in rotated structures and for most of these complexes the computed carbonyl stretching frequencies are found to be very close to that of the native enzyme.

From the above discussions, we have seen that a fully inverted square pyramidal geometry is obtained for the complexes with chelated NHC ligands. To unravel the role of chelation toward stabilizing the rotated geometry, we have performed an in depth molecular orbital analysis for both monodentate and chelated CAAC complexes (i.e., **1_H**-CAAC and **2_H**-CAAC) as a representative case and the results are discussed below.

The rotation of Fe_d(CO)₃ unit in the chelated complexes is a consequence of significant increase in electron density at the proximal iron center. In case of the monodentate complexes, there is a minor difference in the interaction of one of the CAAC ligands with the proximal iron center compared to the other which may be attributed to the difference in spatial orientation of

both the CAACs. However, the restricted rotation of the CAAC ligands upon chelation results in stronger overlap between the carbene lone pair orbitals and vacant d-orbital of the iron center which is further corroborated by the calculated shorter $\text{Fe}_p\text{-C}_c$ bond lengths for the chelated complexes compared to those with monodentate ones. A closer look at Figure 3 shows that in **1H-CAAC**, the lone pair orbital of one of the CAAC ligands weakly overlap with metal vacant d-orbital while both the donor sites interact equally in **2H-CAAC** thereby forming two equal $\text{Fe}_p\text{-C}_c$ bonds. Further, the increase in electron density at the proximal iron center upon chelation of the CAACs (i.e., in **2H-CAAC**) is also evident from an increase in the values of natural charge (-0.284) and natural valence population (8.222) at Fe_p compared to those in **1H-CAAC** (-0.117 and 8.064 respectively). The electron rich proximal iron center undergoes electronic relaxation by transferring some of the excess electron density to one of the basal CO group at Fe_d thereby bringing this CO group to a semi-bridging position (Figure 4). Similar results are also obtained for all other complexes having a rotated geometry at the distal iron center.

In summary, we have designed a number of [FeFe]-hydrogenase model complexes with a variety of structurally and electronically different heterocyclic carbenes at one of the iron centers and investigated their structural and electronic features. We have considered the monodentate as well as the chelated versions of the cyclic carbenes and interestingly, installation of chelated carbenes at the proximal iron center results in the stabilization of rotated conformation at the distal iron center for the reduced Fe(I)Fe(I) state. The stabilization of the completely inverted square pyramidal geometry at the distal iron center is found to be a consequence of significant increase in electron density at the proximal iron center rendered by the presence of chelated carbenes.

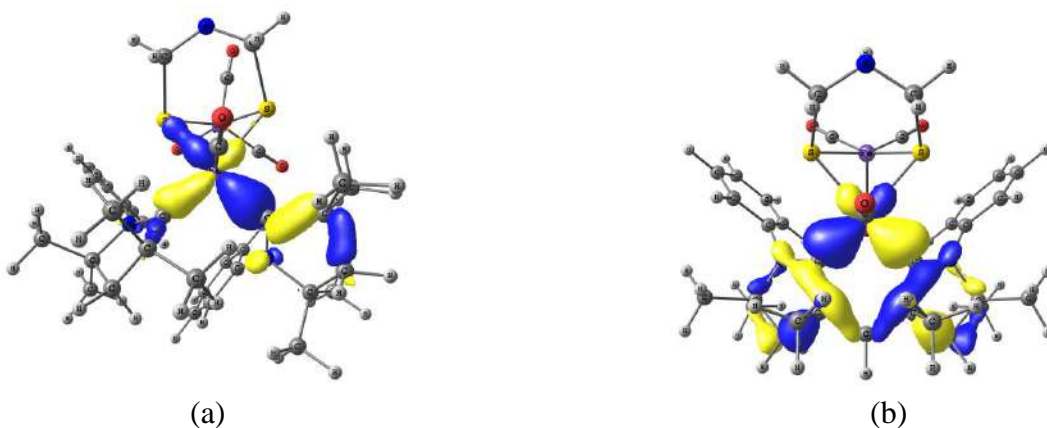


Figure 3: Molecular orbital representing the overlap between the CAAC lone pairs and metal d-orbitals in (a) **1H-CAAC** and (b) **2H-CAAC**.

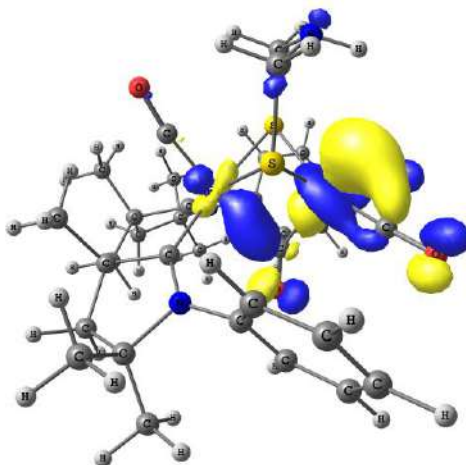
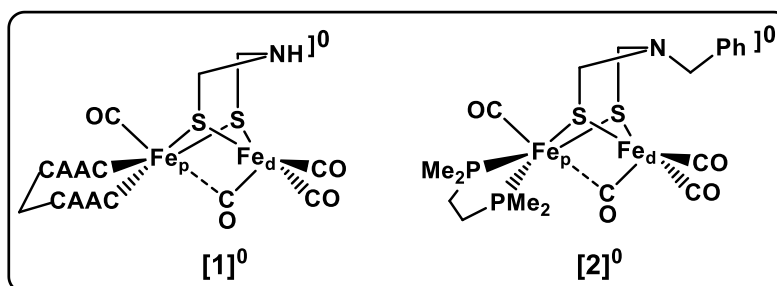


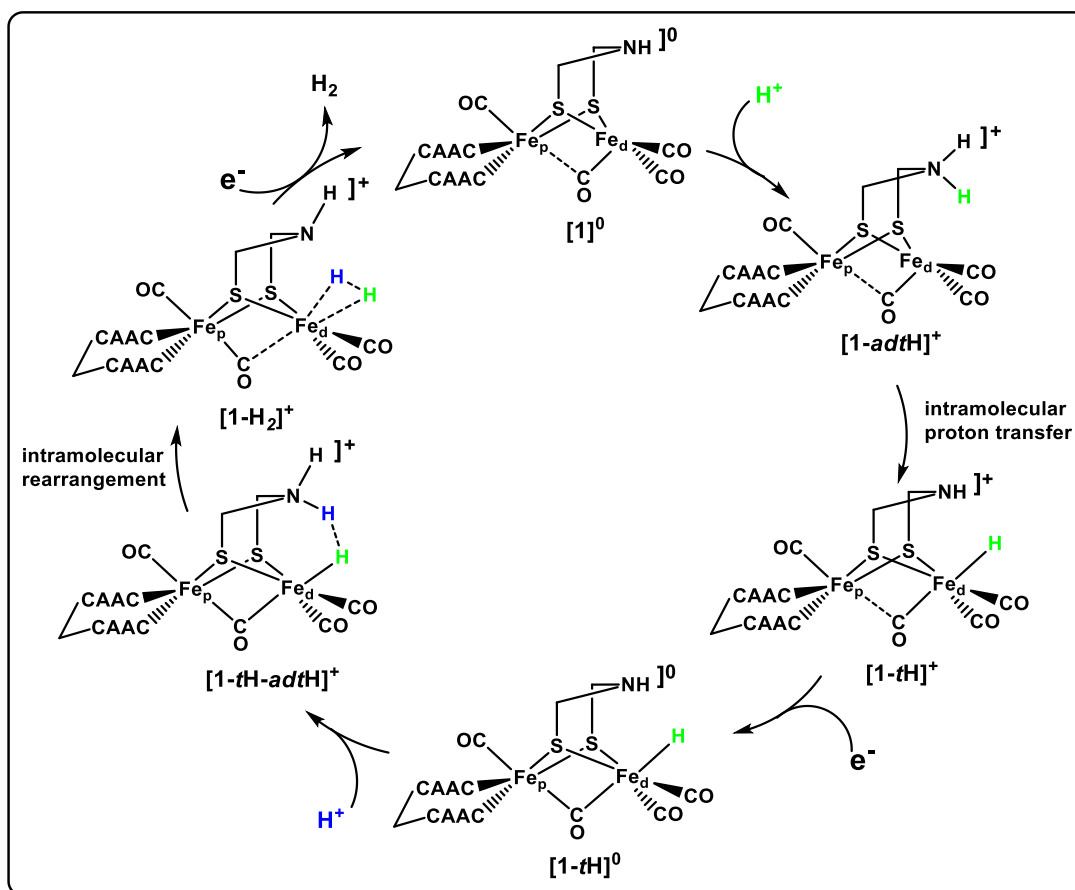
Figure 4: Molecular orbital showing the interaction between the proximal iron center (Fe_p) and bridging carbonyl group in **2H-CAAC**.

After fulfilling the first two objectives, we then turned to the last objective of catalytic formation of dihydrogen by carbene decorated [FeFe]-hydrogenase model complexes and compare the energetics of the catalytic cycle with that of an experimentally known model complex. The carbene decorated complex is denoted by $[1]^0$ while the experimentally known one with dmpe (1,2-bis(dimethylphosphino)ethane) ligand is named as $[2]^0$ (Scheme 4).



Scheme 4: Schematic representation of the model complexes used as catalyst in the present study for production of dihydrogen.

The structural flexibility of the active site of the native [FeFe]-hydrogenase plays a crucial role during reversible reduction of protons to molecular hydrogen. Interestingly, the starting complex $[1]^0$ adopts an inverted square pyramidal geometry at one of the iron centers (Scheme 4) and results in the evolution of molecular hydrogen upon alternate addition of two equivalents of protons and electrons as shown in Scheme 5. Even though the first protonation may directly lead to the terminal hydride $[1\text{-}t\text{H}]^+$, one cannot rule out the possibility of azadithiolate protonation (i.e., protonation at the bridgehead nitrogen atom) as the reaction is found to be exergonic (*vide infra*). Initial protonation leads to an increase in $\text{Fe}_p\text{-Fe}_d$ bond length by 0.02 Å (Table 1) as well as decrease in the extent of bridging of the carbonyl group as evident



Scheme 5: Schematic representation of the catalytic cycle of H₂ production catalyzed by [1]⁰.

from an increase in Fe_p-CO_{bridg} bond length which is further corroborated from an increase in carbonyl stretching frequency (by 58cm⁻¹) for this semi-bridging CO group. The second step involves intramolecular proton transfer from the azadithiolate bridgehead nitrogen atom to the vacant apical site of the distal iron center thereby forming a terminal hydride [1-*t*H]⁺ which is followed by reduction with first equivalent of Cp*₂Cr. A molecular orbital (MO) analysis shows that the lowest unoccupied molecular orbital (LUMO) in [1-*t*H]⁺ has antibonding contribution from both the iron centers (Figure 5) and accordingly, upon reduction, the Fe_p-Fe_d bond distance gets significantly elongated in [1-*t*H]⁰ compared to that in [1-*t*H]⁺ (Table 1). Further, in [1-*t*H]⁰ the carbonyl group between the iron centers came to a completely bridging position as evident from similar Fe_p-CO_{bridg} and Fe_d-CO_{bridg} bond lengths. The next step is the protonation of [1-*t*H]⁰ at the bridgehead nitrogen atom thereby generating an ammonium hydride ([1-*t*H-*adt*H]⁺) which is accompanied by a slight increase in Fe_p-Fe_d bond distance (~0.02Å). It should be noted that the shift in ν_{CO} value for the bridging CO group (23 cm⁻¹) as a result of N-protonation (i.e., [1-*t*H]⁰ vs [1-*t*H-*adt*H]⁺) is comparable to that observed experimentally (20 cm⁻¹) in similar systems. Further, in this diprotonated species, the computed dihydrogen distance (1.552 Å) is comparable to the previously reported value (1.55 Å) and lies within twice the van der Waals radius of hydrogen thereby indicating dihydrogen bonding. In the next step, [1-*t*H-*adt*H]⁺

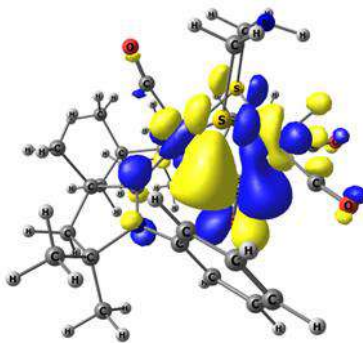


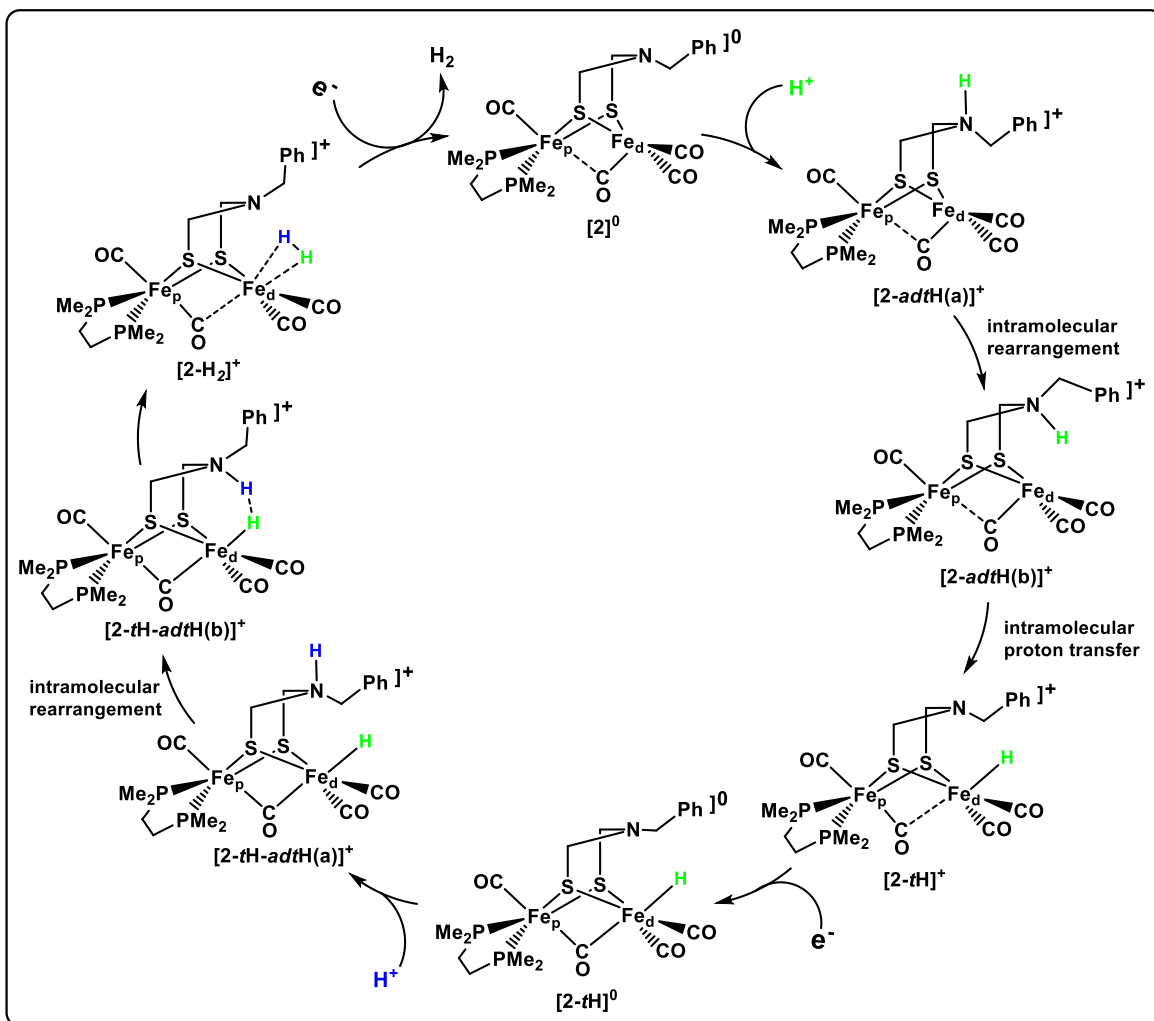
Figure 5: Lowest Unoccupied Molecular Orbital (LUMO) of $[1-tH]^+$.

undergoes rearrangement resulting in the formation of a non-classically bonded dihydrogen complex ($[1-H_2]^+$). The major structural change during this rearrangement is the significant elongation of the Fe_p-Fe_d bond distance as well as shifting of the bridging CO to a semi-bridging position where it strongly binds to Fe_p rather than Fe_d . The catalytic cycle is completed with the liberation of H_2 and regeneration of the catalyst $[1]^0$ upon addition of the second equivalent of reductant (Cp^*_2Cr).

We have also considered the experimentally known complex $[2]^0$ and studied the complete catalytic cycle of H_2 evolution using this complex. The steps involved in case of $[2]^0$ (Scheme 6) are quite similar to those considered for $[1]^0$. The first step is the *N*-protonation at the azadithiolate bridgehead which results in the formation of the ammonium complex ($[2-adtH(a)]^+$). However, unlike in $[1-adtH]^+$, the proton occupies an equatorial position in $[2-adtH(a)]^+$. Therefore, this catalytic cycle involves an additional step where $[2-adtH(a)]^+$ undergoes rearrangement to an intermediate ($[2-adtH(b)]^+$) in which the proton is suitably placed for transfer to Fe_d atom favoring the formation of terminal hydride ($[2-tH]^+$). In $[2-tH]^+$, the Fe_p-Fe_d bond length is significantly longer than that in $[2-adtH(a)]^+$ and $[2-adtH(b)]^+$. However, unlike in $[1-tH]^+$, in $[2-tH]^+$ the semi-bridging CO is strongly bonded to Fe_p rather than Fe_d . This may be attributed to the stronger interaction between Fe_d and the apical hydrogen atom in $[2-tH]^+$ compared to that in $[1-tH]^+$ (Table 1). Further, the stronger interaction between the semi-bridging carbonyl and Fe_p in $[2-tH]^+$ is also supported by the increase in Fe_p-CO_{ap} bond length. Addition of the first equivalent of the reductant (Cp^*_2Cr) leads to the formation of $[2-tH]^0$ which yields the ammonium hydride ($[2-tH-adtH(a)]^+$) upon treatment with proton source ($HBF_4 \cdot Et_2O$). This is followed by rearrangement of the azadithiolate bridge thereby bringing the equatorial hydrogen atom to a position in which it can effectively interact with the terminal hydride ($[2-tH-adtH(b)]^+$). The $H \cdots H$ bond distance in $[2-tH-adtH(b)]^+$ (1.565 Å) is comparable to that computed for $[1-tH-adtH]^+$ (1.552 Å). Both protonation of $[2-tH]^0$ as well as rearrangement of $[2-tH-adtH(a)]^+$ to $[2-tH-adtH(b)]^+$ are found to shift the ν_{CO} value for the bridging CO by almost 18 cm^{-1} to higher energy. Similar to the case with $[1]^0$, here also we could get an intermediate where the dihydrogen molecule is non-classically bonded to the distal iron center ($[2-H_2]^+$) which upon reduction results in the formation of free H_2 as well as regeneration of the catalyst $[2]^0$.

Table 1: M062X/Def2-TZVP calculated values of key geometrical parameters for both the complexes $[1]^0$ and $[2]^0$ and the intermediates involved in the catalytic cycle. The iron centers are denoted by Fe_p and Fe_d whereas the apical and bridging carbonyl groups are indicated by CO_{ap} and CO_{bridg} respectively. The bond lengths are given in Å.

Complex	Fe_p-Fe_d	Fe_p-CO_{ap}	Fe_p-CO_{bridg}	Fe_d-CO_{bridg}	Fe_d-H	H-H
$[1]^0$	2.617	1.874	2.305	1.771	-	-
$[1-adtH]^+$	2.638	1.887	2.384	1.772	-	-
$[1-tH]^+$	2.755	1.887	2.455	1.952	1.515	-
$[1-tH]^0$	2.860	1.936	2.051	2.115	1.589	-
$[1-tH-adtH]^+$	2.880	1.951	2.063	2.123	1.611	1.552
$[1-H_2]^+$	3.117	1.918	1.939	2.900	2.214 2.182	0.755
$[2]^0$	2.605	1.858	2.188	1.779	-	-
$[2-adtH(a)]^+$	2.608	1.866	2.264	1.767	-	-
$[2-adtH(b)]^+$	2.612	1.865	2.645	1.758	-	-
$[2-tH]^+$	2.743	1.900	1.925	2.443	1.491	-
$[2-tH]^0$	2.811	1.917	2.051	2.078	1.561	-
$[2-tH-adtH(a)]^+$	2.840	1.932	2.027	2.091	1.563	-
$[2-tH-adtH(b)]^+$	2.843	1.932	2.078	2.083	1.607	1.565
$[2-H_2]^+$	3.113	1.910	1.928	2.809	2.154 2.124	0.756



Scheme 6: Schematic representation of the catalytic cycle of H₂ production catalyzed by $[2]^0$.

In addition to the intermediates involved in the catalytic liberation of H₂ using $[1]^0$, we also characterized all the possible transition states and the mechanistic steps are depicted in Figure 6. Our calculations suggest that the catalytic production of H₂ using $[1]^0$ is a highly exergonic ($\Delta G = -73.4 \text{ kcal mol}^{-1}$) process. The first *N*-protonation step leading to the ammonium complex $[1-adtH]^+$ is found to be favourable by $8.0 \text{ kcal mol}^{-1}$ which isomerizes to the terminal hydride $[1-tH]^+$ via a transition state ($TS1_{[1]^0}$) with activation energy barrier of $4.8 \text{ kcal mol}^{-1}$. Interestingly, this intramolecular proton transfer step is also facile as indicated by the calculated negative change in Gibbs free energy by $8.8 \text{ kcal mol}^{-1}$. The next step which is the

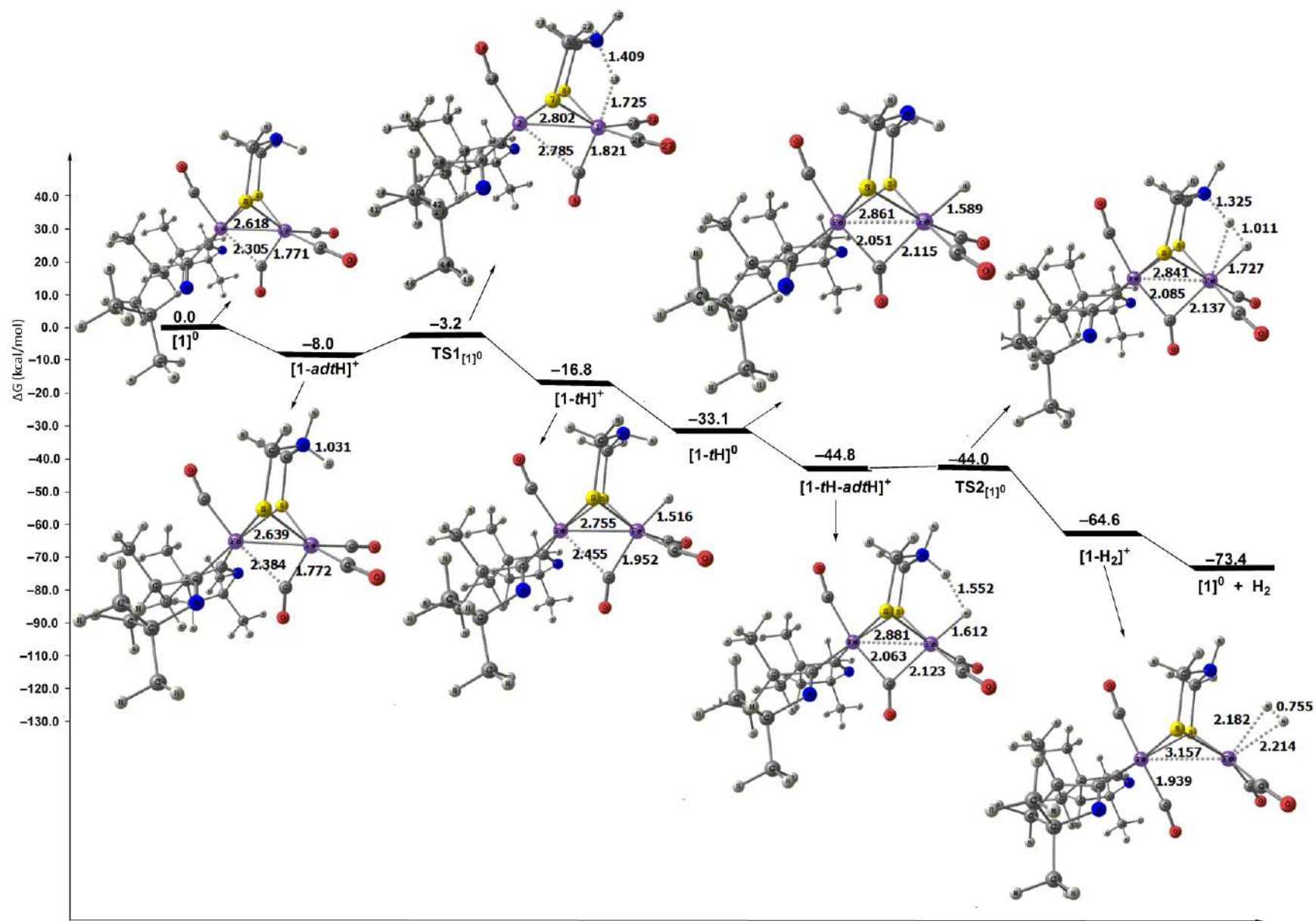


Figure 6: Proposed mechanism for production of H₂ using [1]⁰ (phenyl groups at the nitrogen atoms of CAAC are omitted for clarity.)

reduction with first equivalent of Cp*₂Cr is found to be considerably exergonic with $\Delta G = -16.3$ kcal mol⁻¹. Interestingly, the computed Mulliken spin density values for **[1-tH]**⁰ indicate that ~50% of the total spin is equally distributed on both the iron centers (0.263 and 0.260 on Fe_p and Fe_d respectively) while the remaining 50% is on the bridging carbonyl group (0.503). This equal distribution of spin densities on both the iron centers lead to more symmetric coordination of the bridging CO group in the reduced species. A closer look at Figure 6 indicate that reduction not only increases the Fe_p-Fe_d bond distance in **[1-tH]**⁰ but also significantly increases the Fe_d-H bond length. This can be attributed to the fact that the LUMO of **[1-tH]**⁺ (Figure 5) not only has antibonding interaction between the two iron centers but also has some contribution from the Fe_d-H bond which is antibonding in nature. The second protonation which leads to the formation of the ammonium hydride **[1-tH-adtH]**⁺ is accompanied by an energy release of 11.7 kcal mol⁻¹. This doubly protonated species also maintains the symmetric coordination mode of the bridging CO group which is consistent with nearly equal spin densities on both Fe_p and Fe_d (0.251 and 0.286 respectively) centers. **[1-tH-adtH]**⁺ also features the incipient formation of a dihydrogen bond between the azadithiolate proton and hydride at Fe_d which then undergoes an intramolecular proton transfer to form **[1-H₂]**⁺ through transition state (**TS_{2[1]}**⁰) involving a barrier of only 0.8 kcal mol⁻¹. It should be noted that the energy required to overcome the barrier involved in both the intramolecular proton transfer processes are very minimal thereby indicating the high efficiency of the catalyst **[1]**⁰ toward catalytic production of H₂. While previous studies suggested higher stability for the mixed valence doubly protonated species compared to the weakly bound H₂-adduct, our studies indicate higher stability (by 19.8 kcal mol⁻¹) for the non classically bound dihydrogen complex (**[1-H₂]**⁺) over the isomeric ammonium hydride (**[1-tH-adtH]**⁺). Further, the computed Mulliken spin density values shows that the total spin is entirely localized on the distal Fe center thereby suggesting the mixed valence Fe_p(II)Fe_d(I) oxidation state assignment for **[1-H₂]**⁺ where the H₂ molecule is weakly bonded to a Fe(I) center. Interestingly, the oxidation states of the two iron centers of **[1-H₂]**⁺ resemble that in the H_{ox} state of the native enzyme. Further, in **[1-H₂]**⁺, the bound H₂ has a bond length of 0.755Å which is marginally longer than that for free H₂ molecule (0.740Å, calculated at the same level of theory) suggesting an weakly activated H₂ molecule. The final liberation of H₂ from the loosely bound dihydrogen complex **[1-H₂]**⁺ as a result of addition of second equivalent of reductant is also found to be exergonic by -8.8 kcal mol⁻¹.

For comparison, we have also studied the mechanistic details of catalytic production of H₂ using experimentally characterized **[2]**⁰ and the steps are depicted in Figure 7. The initial N-protonation as well as subsequent isomerization to **[2-adtH(b)]**⁺ are found to be exergonic in nature (by -1.0 and -4.4 kcal mol⁻¹ respectively). It should be noted that while the Fe_d center adopts a complete inverted square pyramidal geometry in both **[2]**⁰ and **[2-adtH(b)]**⁺, the same is distorted to some extent in **[2-adtH(a)]**⁺. This may be attributed to the absence of agostic interaction between the bulky azadithiolate substituent and the distal iron center which is responsible for the stabilization of the rotated structure in Fe(I)Fe(I) state. The terminal hydride

formation is found to be favourable by 1.4 kcal mol⁻¹ which involves a transition state (**TS1**_{[2]⁰}) with an activation energy barrier of 9.2 kcal mol⁻¹. A comparison with Figure 6 shows that the energy barrier for this intramolecular proton transfer is higher in **[2]**⁰ compared to that in **[1]**⁰. However, reduction of the terminal hydride (**[2-tH]**⁺) is computed to be more exergonic ($\Delta G = -21.1$ kcal mol⁻¹) as compared to that in **[1]**⁰ ($\Delta G = -16.3$ kcal mol⁻¹) which may be attributed to the electron rich nature of the diiron core in **[1]**⁰ rendered by the presence of better electron donating chelated CAAC ligands. Further, as evident from the calculated Mulliken spin densities the distribution of the total spin in **[2-tH]**⁰ (~ 50% on both the iron centers and ~ 50% on the bridging CO) is akin to that in **[1-tH]**⁰. Similar to the first protonation, the formation of the doubly protonated species (**[2-tH-adtH(a)]**⁺) is also marginally exergonic ($\Delta G = -1.1$ kcal mol⁻¹). However, the isomerisation of **[2-tH-adtH(a)]**⁺ to **[2-tH-adtH(b)]**⁺ is significantly exergonic in nature ($\Delta G = -12.6$ kcal mol⁻¹). This is followed by an intramolecular proton transfer process involving **TS2**_{[2]⁰} which leads to the weakly bound dihydrogen complex **[2-H₂]**⁺. Interestingly, similar to the case with **[1]**⁰, here also the formation of this non-classical dihydrogen complex **[2-H₂]**⁺ is almost a barrier less process ($\Delta G^\ddagger = +2.3$ kcal mol⁻¹). Further, the H...H bond length in **[2-H₂]**⁺ is 0.756 Å which is equal to that obtained in **[1-H₂]**⁺. Similar to **[1-H₂]**⁺, **[2-H₂]**⁺ also contains a mixed valence Fe(II)Fe(I) core as indicated by the calculated Mulliken spin density values (0.014 on Fe_p and 1.118 on Fe_d).

Further, in order to investigate the redox behaviour of the singly and doubly protonated species of both **[1]**⁰ and **[2]**⁰, we have calculated the reduction potentials (Table 2) for both the reduction event involved in the catalytic cycle. The calculated reduction potential for the couple **[1-tH]**⁺/**[1-tH]**⁰ is found to be significantly negative compared to that computed for the second reduction event (**[1-H₂]**⁺/**[1]**⁰). This indicates that the reduction of the weakly bound dihydrogen complex is more favourable compared to the terminal hydride species.

Table 2: BP86/Def2-TZVP calculated values of reduction potentials of the reduction events for both **[1]**⁰ and **[2]**⁰.

Redox Event	E^\bullet (eV)
[1-tH] ⁺ / [1-tH] ⁰	-1.41
[1-H₂] ⁺ / [1] ⁰	0.10
[2-tH] ⁺ / [2-tH] ⁰	-1.32
[2-H₂] ⁺ / [2] ⁰	0.26

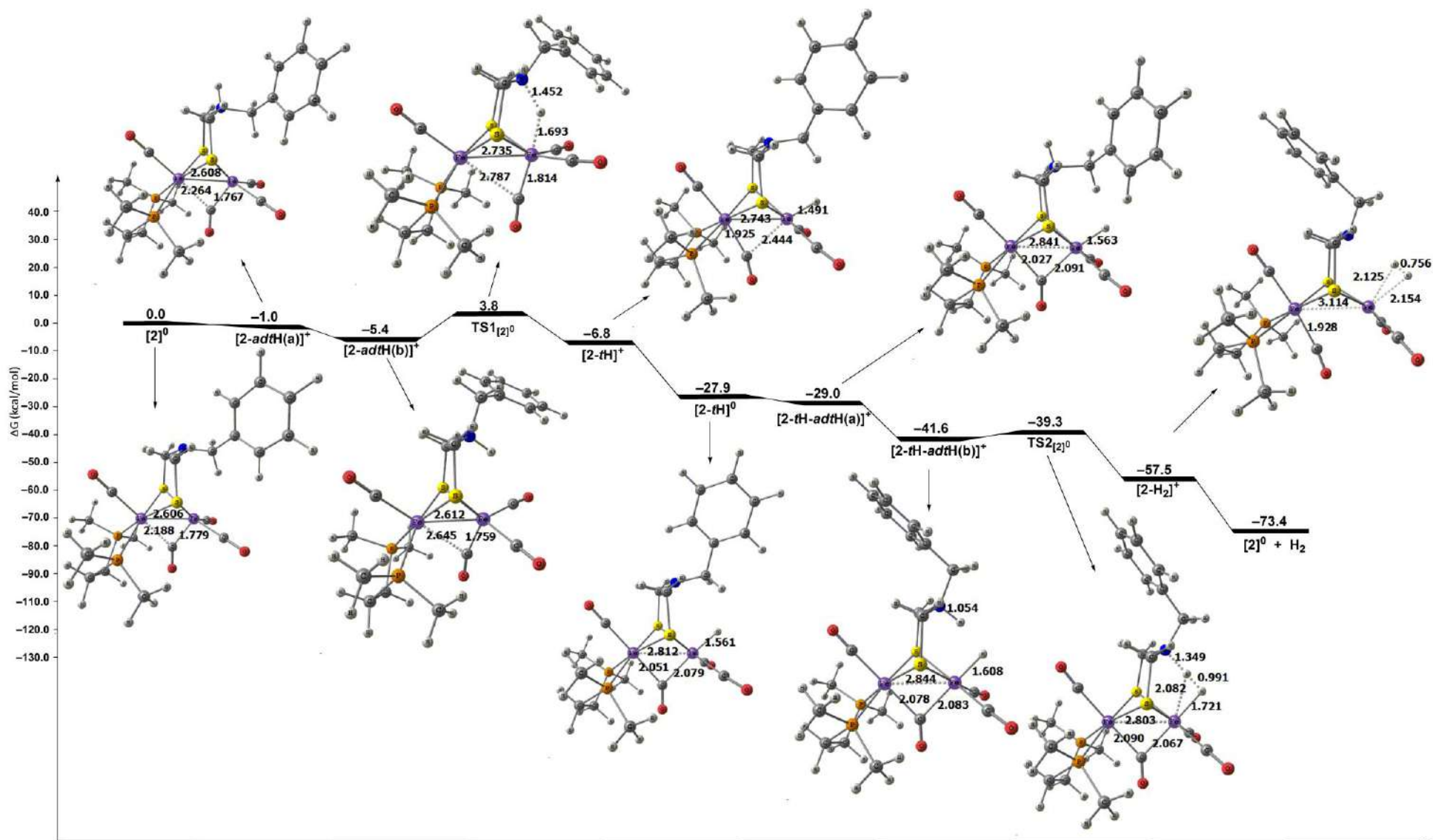


Figure 7: Proposed mechanism for production of H₂ using [2]⁰.

Similar results are also obtained for the redox couples with the dmpe substituted complex (**[2]⁰**). However, the E° values calculated for the reduction events involved in the catalytic cycle of **[1]⁰** are found to be less positive compared to those for **[2]⁰**. This can be reasoned to the presence of chelated CAAC ligands in **[1]⁰** which renders the diiron core more electron rich compared to that in **[2]⁰**. It should be noted that our calculated potential values for the reduction of the terminal hydride species in both **[1]⁰** and **[2]⁰** are comparable, indeed more favourable (*i.e.*, less negative) than those reported for similar experimentally known system.


In summary, we performed quantum chemical calculations to understand the mechanistic details of catalytic production of dihydrogen using bio-inspired [FeFe]-hydrogenase model complexes which possess rotated conformation at one of the iron centers. The catalytic evolution of H₂ is found to be highly favourable using both the complexes as evident from high exergonicity of the overall reaction as well as very shallow activation energy barrier for the transition states involved. Interestingly, on the basis of computed Mulliken spin density values, this study provides evidence for an intermediate where dihydrogen is non-classically bonded to an iron center (Fe_d) with the total spin entirely localized on Fe_d. Most importantly, the computed reduction potential values for the model systems are found to be less negative compared to that reported earlier for experimentally known system. In accordance with previous experimental observations, our calculations also demonstrate the higher basicity of the distal iron center compared to the amino nitrogen atom. However, one cannot completely rule out the possibility of the amino group of the azadithiolate bridge as the initial protonation site. We hope our study will inspire synthetic chemists towards dihydrogen production employing carbene anchored biomimetic [FeFe]-hydrogenase model complexes.

ANNEXURE-II

Consolidated Statement of Accounts (From the date of commencement)													
Scheme Numer		: 01(2912)/17/EMR-II dated 03-05-2017											
Title of the Research Scheme: Computational Design of Functional and Structural Mimics of the Active Site of [FeFe]-Hydrogenase													
Name of The Principal Investigator: Prof. Ashwini K. Phukan													
Date of Commencement: 01-06-2017										Date of Termination: 31-05-2020			
Receipts (Particulars of grants received)							Payments (Particulars of grants spent)						
Period (April-May, 2020)	Check No.- Date -- Amount-	Contingency (Rs) Opening Balance	Scientist Allowance(For Emeritus Scientist Only)	Equipment Grant (Rs)	HRA + MA	Bank Interest Accrued during 01-04-2020 to 31-05-2020 (Rs)	Total (Rs)	Contingency (Rs)	Scientist Allowance(For Emeritus Scientist Only)	Equipment Grant (Rs)	HRA + MA	Total (Rs)	Balance (Rs)
01-04-2020 to 31-05-2020	NA	57,537.00	NA	Nil	NA	Nil	57,537.00	Nil	NA	Nil	NA	Nil	57,537.00

Name: 
(Registrar, Tezpur University)

Name: 
(Finance Officer)


07/10/21
Prof. Ashwini K. Phukan
(PI)

Registrar
Tezpur University

Finance Officer
Tezpur University



FORM-L
UTILISATION CERTIFICATE

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
Human Resource Development Group
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

Name of the Project: Computational Design of Functional and Structural Mimics of the Active Site of [FeFe]-Hydrogenase

CSIR-HRDG Scheme No: 01(2912)/17/EMR-II dated 03-05-2017

PI: Prof. Ashwini K. Phukan, Dept. of Chemical Sciences, Tezpur University, Napaam, Assam-784028

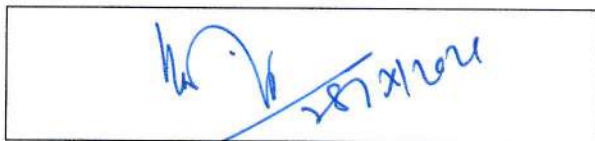
S.No.	Particulars	Letter No. /Bank Transaction ID Nos. & Date	Amount (Rs.)
1	Grants received from CSIR during the year	Nil	57,537.00 (Opening balance of Rs. 57,537.00)
2.	Interest earned/accrued on CSIR grant	----	Nil
3.	Amount utilized during April 01, 2020 to May 31, 2020	----	Nil
4.	Unspent balance as on May 31, 2020 [(1) + (2) –(3)]	----	57,537.00

1. Certified that out of **Rs. Nil** of grant-in-aid released by Extramural Research (EMR) Division of HRDG (CSIR) and opening balance of **Rs. 57,537.00 (Rupees Fifty Seven Thousand Five Hundred Thirty Seven only)** as mentioned in the Table given above for the time duration of April 01, 2020 to May 31, 2020 and **Rs. Nil** earned/accrued as interest from bank on grants released by CSIR, a sum of **Rs. Nil** has been utilized and that the balance of **Rs. 57,537.00 (Rupees Fifty Seven Thousand Five Hundred Thirty Seven only)** remaining unutilized at the end of the year has been returned to the funding agency vide two numbers of Demand Drafts (**DD No. 535350 dated 04.10.2021 for an amount of Rs. 54,234/- & DD No. 535178 dated 16.06.2021 for an amount of Rs. 3,303/-**).

2. Certified that I have satisfied myself that the conditions on which the grants-in-aid was sanctioned are being fulfilled and that I have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned. The detail expenditure incurred during the year is shown in the enclosed "Statement of Accounts (Receipt & Payment)".

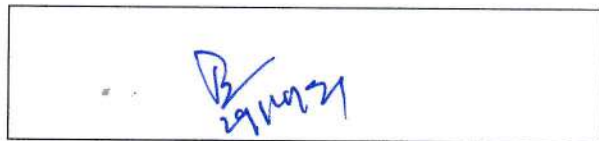
(Kinds of checks exercised)

1. Vouchers and Statement of Accounts
2. Grant-in-Aid
3. Expenditure Register
4. Bank statements for accrual interest



Signature of Authorised Officer
with Date & Seal

Finance Officer




Countersigned by Registrar/Dean/Director
Of the institute with Date & Seal

Registrar


The Utilization certificate and statement should be signed by Head of the Department/Accounts and countersigned by Registrar/Dean/Director of the University/Institute.

ANNEXURE-II


Consolidated Statement of Accounts (From the date of commencement)													
Scheme Numer		: 01(2912)/17/EMR-II dated 03-05-2017											
Title of the Research Scheme: Computational Design of Functional and Structural Mimics of the Active Site of [FeFe]-Hydrogenase													
Name of The Principal Investigator: Prof. Ashwini K. Phukan													
Date of Commencement: 01-06-2017							Date of Termination: 31-05-2020						
Receipts (Particulars of grants received)							Payments (Particulars of grants spent)						
Period (Ending 31 st March)	Check No.- Date – Amount-	Contingency (Rs) Opening Balance	Scientist Allowance(For Emeritus Scientist Only)	Equipment Grant (Rs)	HRA + MA	Bank Interest Accrued during 01-04-2019 to 31-03-2020 (Rs)	Total (Rs)	Contingency (Rs)	Scientist Allowance(For Emeritus Scientist Only)	Equipment Grant (Rs)	HRA + MA	Total (Rs)	Balance (Rs)
01-04-2019 to 31-03-2020	NA	55,861.00	NA	Nil	NA	1,676.00	57,537.00	Nil	NA	Nil	NA	Nil	57,537.00

Name: 
(Registrar, Tezpur University)

Registrar
Tezpur University

Name: 
(Finance Officer)

Finance Officer
Tezpur University


Prof. Ashwini K. Phukan
(PI)



FORM-L
UTILISATION CERTIFICATE

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
Human Resource Development Group
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

Name of the Project: Computational Design of Functional and Structural Mimics of the Active Site of [FeFe]-Hydrogenase

CSIR-HRDG Scheme No: 01(2912)/17/EMR-II dated 03-05-2017

PI: Prof. Ashwini K. Phukan, Dept. of Chemical Sciences, Tezpur University, Napaam, Assam-784028

S.No.	Particulars	Letter No. /Bank Transaction ID Nos. & Date	Amount (Rs.)
1	Grants received from CSIR during the year	Nil	55,861.00 (Opening balance of Rs. 55,861.00)
2.	Interest earned/accrued on CSIR grant	----	1,676.00
3.	Amount utilized during April 01, 2019 to March 31, 2020	----	Nil
4.	Unspent balance of April 01, 2019 to March 31, 2020 [(1) + (2) –(3)]	----	57,537.00

1. Certified that out of Rs. Nil of grant-in-aid released by Extramural Research (EMR) Division of HRDG (CSIR) and opening balance of Rs. 55,861.00 (Rupees Fifty Five Thousand Eight Hundred Sixty One only) as mentioned in the Table given above for the time duration of April 01, 2019 to March 31, 2020 and Rs. 1,676.00 (Rupees One Thousand Six Hundred Seventy Six only) earned/accrued as interest from bank on grants released by CSIR, a sum of Rs. Nil has been utilized and that the balance of Rs. 57,537.00 (Rupees Fifty Seven Thousand Five Hundred Thirty Seven only) remaining unutilized at the end of the year will be adjusted towards the grant-in-aid payable during the next period i.e. April, 2020 – May, 2020.

2. Certified that I have satisfied myself that the conditions on which the grants-in-aid was sanctioned are being fulfilled and that I have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned. The detail expenditure incurred during the year is shown in the enclosed "Statement of Accounts (Receipt & Payment)".


(Kinds of checks exercised)

1. Vouchers and Statement of Accounts
2. Grant-in-Aid
3. Expenditure Register
4. Bank statements for accrual interest



Signature of Authorised Officer
with Date & Seal

Finance Officer
Tosapur University



Countersigned by Registrar/Dean/Director
Of the institute with Date & Seal

Registrar
Tosapur University

The Utilization certificate and statement should be signed by Head of the Finance & Accounts and countersigned by Registrar/Dean/Director of the University/Institute.

भारतीय स्टेट बैंक
State Bank of India

Issuing Branch: TEZPUR UNIVERSITY
Branch Code No: 14259
Branch No: 03712-267285

Key: TEJDUR
Sr. No: 53810

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मांगदृष्टपत्र
DEMAND DRAFT

मांगे जानेपर THE DEPUTY SECRETARY EXTRAMURAL RESEARCH, CSIR COMPLEX

ON DEMAND PAY
रुपये RUPEES
Three Thousand Three Hundred and Three Only

अदा करें ₹ 3303.00

IOI 000471535178
Name of Applicant
TEZPUR UNIVERSITY R & D

AMOUNT BELOW 3304(0/4)

रुपय प्राप्त / VALUE RECEIVED

कागज़ पर मुद्रित होने पर ही वैध
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भारतीय स्टेट बैंक
STATE BANK OF INDIA

प्राधिकृत हस्ताक्षरकर्ता
AUTHORISED SIGNATORY

शाखा प्रबंधक
BRANCH MANAGER

अदाकर्ता शाखा / DRAWEE BRANCH: NEW DELHI MAIN BRANCH
कोड नं. / CODE No: 00691

INSTRUMENTS FOR ₹ 1,50,000- & ABOVE ARE NOT VALID UNLESS SIGNED BY TWO OFFICERS

SATYAJIT MAZUMDAR
M 13712

॥ 535172 ॥ 00002000 ॥ 000471 ॥ 16

भारतीय स्टेट बैंक
State Bank of India

Issuing Branch: TEZPUR UNIVERSITY
Branch Code No: 14259
Branch No: 03712-267285

Key: VIKLAS
Sr. No: 784679

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मांगदृष्टपत्र
DEMAND DRAFT

मांगे जानेपर THE DEPUTY SECRETARY, EXTRAMUR L RESEARCH, CSIR, CSIR COMPLE

ON DEMAND PAY X
रुपये RUPEES
Fifty Four Thousand Two Hundred and Thirty Four Only

अदा करें ₹ 54234.00

IOI 000471535350
Name of Applicant
TEZPUR UNIVERSITY R & D

AMOUNT BELOW 54235(0/5)

रुपय प्राप्त / VALUE RECEIVED

कागज़ पर मुद्रित होने पर ही वैध
VALID ONLY IF COMPUTER PRINTED

केवल 3 महीने के लिए वैध
VALID FOR 3 MONTHS ONLY

भारतीय स्टेट बैंक
STATE BANK OF INDIA

प्राधिकृत हस्ताक्षरकर्ता
AUTHORISED SIGNATORY

शाखा प्रबंधक
BRANCH MANAGER

अदाकर्ता शाखा / DRAWEE BRANCH: NEW DELHI MAIN BRANCH
कोड नं. / CODE No: 00691

INSTRUMENTS FOR ₹ 1,50,000- & ABOVE ARE NOT VALID UNLESS SIGNED BY TWO OFFICERS

॥ 535350 ॥ 00002000 ॥ 000471 ॥ 16