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Electronic Structure Engineering of Transition Metal Nitrides with Computational Chemistry

DAAD

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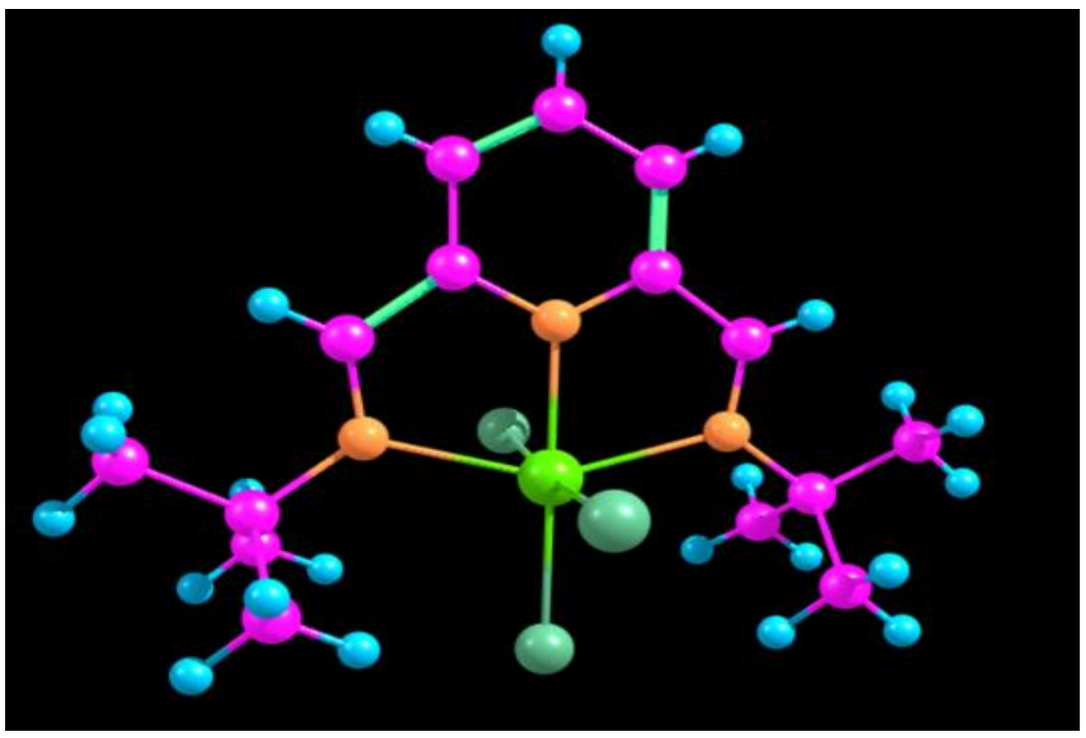
1. Introduction

Nitrogen is a vital element for all the living forms on the planet. Since most of the nitrogen exists as inert N_2 gas, fixing of molecular N_2 is necessary. Currently nitrogen is reduced to ammonia industrially using Haber-Bosch process, which is quite energy intensive. The motive of our research project was to develop alternative paths towards ammonia production using theoretical chemistry. Transformation of N_2 gas can be achieved by using transition metal–N_2 complexes as catalysts.

This report covers the systematic computational chemical study of the individual steps of metal nitride protonation, that is identifying the energetic landscape en route to ammonia production.

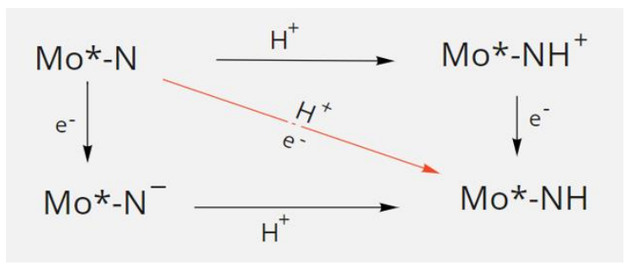


2. Supervised Complex Compound

Complex formula: $MoC_{15}N_3H_{23}Cl_3$ (denoted by Mo*). The compounds can be structured in two ways: cis-chloride complex and trans-chloride complex.

2 (Mo*-Cl) → Mo*-N ≡ N-Mo* → 2 (Mo* ≡ N)

Reaction Mechanism:



3. Optimization and Energy calculations

All the compounds were optimized and run for energy calculations using the Lichtenberg cluster. Δ Electronic Energy, Δ G and Δ H values were computed and analyzed for all the intermediate reactions. As we go across the pathway, i.e., from Mo*N to Mo^*NH_3, electronic energy decreases for every step.

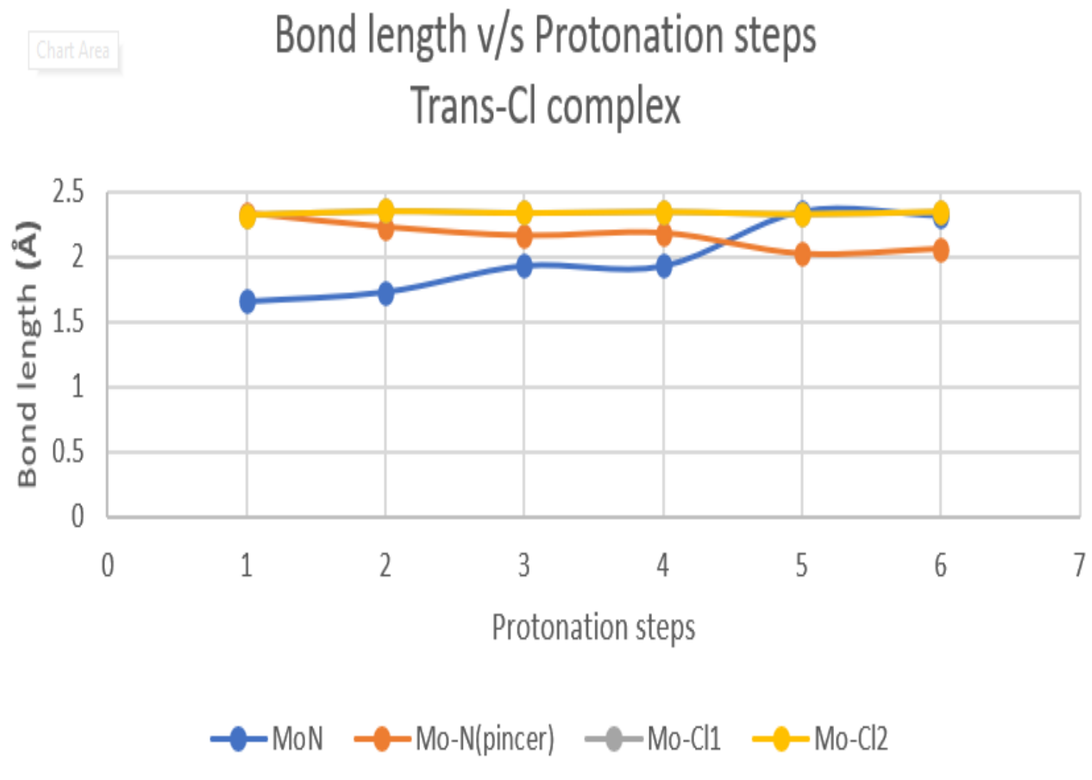
References:

1. Ashida, Y. & Nishibayashi, Y. *Chem. Commun., (2021)* DOI: 10.1039/D0CC07146C.
2. Coe, B.J. & Glenwright, S.J. Trans-effects in octahedral transition metal complexes. *Coordination Chemistry Reviews 203 (2000) 5-80*.

4. Comparison of bond parameters

Bond lengths and bond angles surrounding the central metal ion were computed for both cis-chloride and trans-chloride structures.

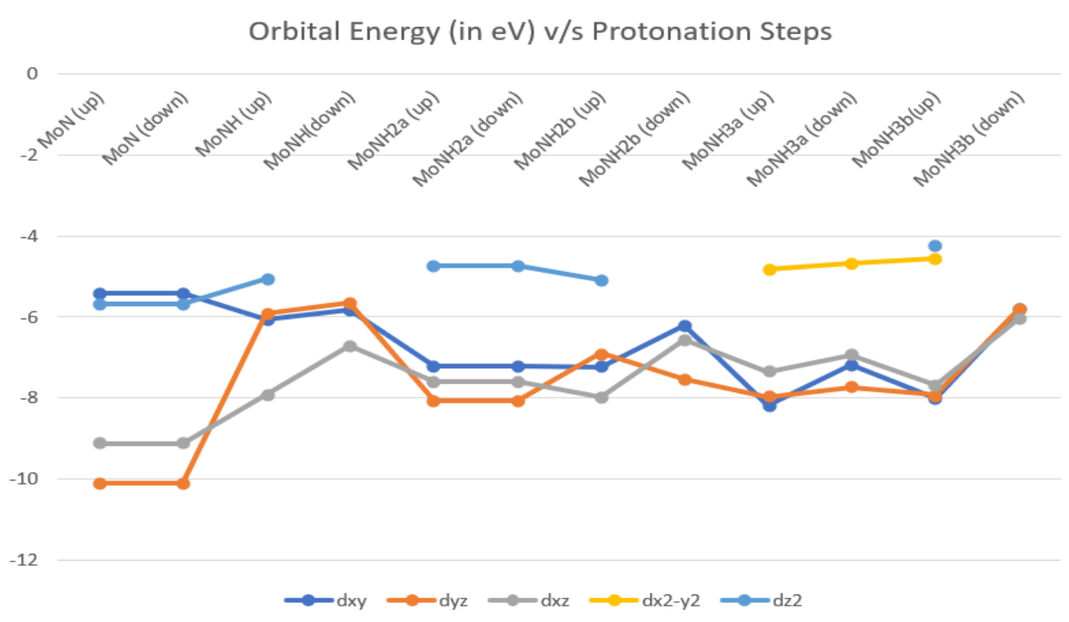
MoN bond length increases significantly as we go from Mo*N to Mo^*NH_3. No major changes were noticed in other bond lengths and bond angles.



5. Orbital energy v/s Protonation steps

Orbital energies for dxy, dyz, dxz, dx^2-y^2, dz^2 were calculated and plotted against the protonation steps. For the trans-chloride structure, energy of dxy orbital decreases across the pathway, indicating stabilization.

Energy of dyz, dxz, dx^2-y^2 and dz^2 orbitals increases across the pathway, indicating decrement in stability.



6. Conclusions

All the intermediate reaction steps are exothermic and exergonic. For all the compounds except Mo^*NH_3 (with multiplicity=2), trans structure is more stable than cis structure in terms of both; electronic energy and bonding parameters.

This complex has a great potential to be researched further as an efficient ammonia production catalyst.