

Computational mechanistic study of the water reduction reaction by cobalt catalysts based on aminopyridine ligands

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Water splitting reaction promoted by sunlight is the most widely desired energetic pathway for hydrogen production and was recognized as a convenient solution to solve the long-run storage of renewable energies through a particularly clean way. Running this reaction is a difficult task and more challenging is the discovery of molecules that efficiently catalyze the reduction of protons to H₂.¹ The iron and nickel hydrogenase enzymes present in some microbial organisms produce H₂, but they are instable under aerobic conditions and suffer from high costs, making difficult their application in solar-driven water-splitting devices for H₂ production.²

Many efforts have been done to develop biomimetic catalytic systems capable to produce molecular hydrogen, but usually such catalysts tend to decompose in presence of molecular oxygen and operate at relatively high negative potentials.³ On the other hand, in the last years an intense search has been dedicated to the development of hydrogen evolution catalysts based on earth-abundant transition metals capable to catalyse the reduction of protons to H₂ at low overpotentials or by using light as a source of energy. Molecular complexes based on first row transition metals like cobalt,⁴ nickel,⁵ iron⁶ and molybdenum⁷ have been shown to be catalytically active on the reduction reaction of the protons from water (WR) to H₂ under electro- and photochemical conditions in an efficient manner. Fundamental understanding of metal catalysed WR mechanisms at molecular scale is essential for its development.

Recently, our group has reported the synthesis, characterization and WR activity of new cobalt, nickel and iron aminopyridine complexes based on the pentadentate ligand 1,4-di(picolyl)-7-(*p*-toluenesulfonyl)-1,4,7-triazacyclononane (Py₂^{Ts}tacn).⁸ All three complexes have excellent electrocatalytic proton reduction activity in acetonitrile, when using trifluoroacetic acid, while only cobalt complexes are active under photochemically conditions (in water) using an iridium photosensitizer. In order to understand how these cobalt catalysts work, we have carried DFT calculations to i) identify the catalytic active species; ii) to propose a viable catalytic cycle for the mechanism of photochemically driven H₂ generation from water⁹ and iii) to elucidate the role of the ligand and the transition metal on the water reduction reaction activity for the aminopyridine complexes.

Quantum mechanical mechanistic analysis supported by experimental data will allow us to understand which factors make feasible the WR process. This information could be used as a guide to synthesize more efficient WR catalysts based on earth-abundant materials.

References:

1. J.L. Dempsey, B.S. Brunschwig, J.R. Winkler, H.B. Gray, *Acc. Chem. Res.* **2009**, *42*, 1995.
2. J.C. Fontecilla-Camps, A. Volbeda, C. Cavazza, Y. Nicolet, *Chem. Rev.* **2007**, *107*, 4273.
3. C. Tard, C.J. Pickett, *Chem. Rev.* **2009**, *109*, 2245.
4. a) V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angew. Chem. Int. Ed.* **2011**, *50*, 7238; b) W.T. Eckenhoff, R. Eisenberg, *Dalton Trans.* **2012**, *41*, 13004.
5. a) M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois, D. L. DuBois, *Science* **2011**, *333*, 863; b) Z. Han, F. Qiu, R. Eisenberg, P. L. Holland, T. D. Krauss, *Science* **2012**, *338*, 1321; c) Z. Han, W. R. McNamara, M.-S. Eum, P. L. Holland, R. Eisenberg, *Angew. Chem. Int. Ed.* **2012**, *51*, 1667.
6. a) F.Gärtner, A. Boddien, E. Barsch, K. Fumino, S. Losse, H. Junge, D. Hollmann, A. Br ckner, R. Ludwig, M. Beller, *Chem. Eur. J.* **2011**, *17*, 6425; b) T. Matsumoto, H.-C. Chang, M. Wakizaka, S. Ueno, A. Kobayashi, A. Nakayama, T. Taketsugu, M. Kato, *J. Am. Chem. Soc.* **2013**, *135*, 8646; c) R. Lomoth, S. Ott, *Dalton Trans.* **2009**, 9952; d) A. M. Kluwer, R. Kapre, F. Hartl, M. Lutz, A. L. Spek, A. M. Brouwer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 10460; e) Y. Na, M. Wang, J. Pan, P. Zhang, B. Åkermark, L. Sun, *Inorg. Chem.* **2008**, *47*, 2805.
7. a) H. I. Karunadasa, C. J. Chang, J. R. Long, *Nature* **2010**, *464*, 1329; b) H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, *Science* **2012**, *335*, 698.
8. A. Call, Z. Codolà, F. Acuña-Parés, J. Lloret-Fillol, *Chem Eur J.* **2014**, *20*, 6171.
9. F. Acuña-Parés, A. Call, J.M. Luis, J. Lloret-Fillol, *unpublished results*.