Second coordination sphere effects in [FeFe]-Hydrogenase mimics

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Acknowledgments
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After about four years, another chapter of my life is now coming to an end. However, this cannot be done without first spending few words of appreciation for those who contributed either directly or indirectly to my work and thesis.

Firstly, I would like to express my gratitude to my supervisor Joost for giving me the opportunity to join the HomKat group and the chance to further explore the fascinating hydrogenase topic under a different perspective than what I was used to. I really appreciated the complete freedom I could experience, being able to explore my own ideas and routes. Thanks for your useful insights and discussions to reconstruct many scientific puzzles.

I am very grateful to my copromotor Jarl. Without you this book would have been very different! Thanks for solving my crystal structures, for your inputs, remarks and attention to the smallest details. In particular, thank you for being extremely patient and always available to help and listen. Among the things I learned from you there is a key lesson: each and every day deserves a new colorful shirt!

Special thanks to Remko for being my second copromotor, but also for being a daily companion always ready to enter an interesting and endless discussion about electrochemistry, devices and so on. I do miss those times when you also were around in the lab. Good luck and all the best for the near future!

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I would now like to express my sincere gratitude to the rest of the committee members Lies Bouwman, Marc Koper, Jan van Maarseveen and Sander Woutersen for making time to read this manuscript and accepting to be part of this important day.

Very special thanks to Tom Rauchfuss for accepting to join the committee and for travelling about 6,000 km to be here. But most importantly thank you for initiating me to the hydrogenase topic and to the academic research in general. I am very grateful for your enthusiasm and motivation without which I probably would have never started a PhD. Looking forward to welcome you in Amsterdam. I really miss our conversations in front of delicious food. This time, I'll bring you to the Dutch version of the Black Dog in Urbana, I am sure you will like it!

A big thanks to my paranymphs Simon and Tessel. Thank you for taking up this difficult task; I am sure you will do just great, looking forward to it. And Tessel... good luck dealing with the Australian! I’m sure you will have a lot of fun, but you will also need a lot of patience.
Next, I want to thank the technicians as their hidden role is essential for research and keeping the labs in good order. Lidy, thank you very much for sharing with me your experience, expertise and most often random, weird and extremely rare pieces of glassware. Thanks for doing your best at keeping all the supplies under control so that the lab could run smoothly. Erik, thanks for solving countless issues, in particular, for every time I brought an issue to your attention and you always solved it in no time. Jan Meine and Ed thanks for keeping the NMR and mass equipment in good order and for getting around my NMR questions and my urgent mass samples. I really appreciated your contribution. Thanks also to Fatna and Taasje.

To my colleagues of E1.41, thanks for creating a nice and friendly work environment. Bart, super nice time at my first conference in Poland. Also I still remember that Saturday when you set on fire my best column. Ping, I had very nice time sharing the apartment with you for few months. Thanks for teaching me your awesome dumpling making technique and for sharing the delicious dumplings afterwards! Hope you can finally enjoy your family and your daughters. Annemarie, my fume hood neighbor and the happiest person I have ever met. Thanks for bringing the sun into the lab, every day with a new song and a new dance. Wojciech, you are the most acknowledged person in my entire thesis. Thanks for solving the structure of most of my crystals and for always sharing your deep chemistry knowledge and your insights. Also thank you for reading all the random papers I used to put at the coffee corner and for getting back to me with your comments! Wish all the best for you, your family and with your new job. Esther S. thanks for the occasional only one beer evenings ending up in deep emotional conversations till 8:00am. Fenna, I still wonder if you ever found that post-it of mine with my birthday wishes for you... I am starting to think it went lost.

Simon, since the very first moment you stepped into our office (and lab) you have been talking about sardines... Lots of bla bla bla but nothing happened yet. So disappointing! I cannot move on to my next chapter without having a taste of this delicious dish of yours. Aside from this, thanks for sharing all the knowledge you have accumulated over the years and thanks a lot for all your valuable TIPS (both the one from Fluorochem and your actual synthetic tips and support during demanding experiments).

René, you were the most helpful person in the entire lab when I joined the group. You always had a good answer to my questions (although 80% of the time your answer was: ask Erik). I am very happy we have shared a lot of nice chemistry, conferences and cooking experiences. Nevertheless, you were also the first person ever giving me a psychological trauma; I now know white asparagus are the real deal and that one must discard not less than 80% of their volume as that part is skin! Anyhow, is it asparagus season, isn’t it?
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Tessel, E1.41 is known for being the smelliest lab of the entire UVA, nevertheless only few know that you actually hold the record for the smelliest compound ever made! I always enjoyed helping you out whenever I could but that day... not so much! Besides this, I remember as it was yesterday (maybe because it actually was yesterday) when I asked you to be my paronymph and you happily and gladly accepted the task. The smile on your face was really flattering. Also, thanks for translating my summary; I feel I owe you a full Sunday of fun at some point!

Pauline, was very nice having you in the lab as your smile and laugh were contagious. Bid, I always have been very jealous of your green and blue air-stable compounds! Joeri, someday I will get you a real birthday present. Good luck with your two-thousand projects. Bradja, you are a machine; so many reactions and columns every day. Was very nice having you in the lab. David, thanks a lot for your endless effort to model my cages, I really appreciate that. I am very positive we can become good friends, I look forward to that but dude, you should talk way slower if you want me to understand you! Vivek, you are not technically part of E1.41 as you don’t need a lab for your simulations, but at least in my mind you are. Thanks for helping me out with the DFT calculations and bearing with my super basic questions. Thanks for sharing your cooking; it’s amazing and I do think that you should be doing that more often. Fengshou, welcome to our lab!

Special thanks to InCatT for letting me use their massive scale glassware which inevitably came with precious suggestions from Sander K. and unspeakable but enjoyable conversations with Zohar.

Thanks to the rest of HomKat members, your contribution was essentials for the nice atmosphere around the lab. Anne, thanks for literally saving my life on few occasions, Christophe, Martin, Andrea, Colet, no more electrolysis? Potentiostat is now always free. Linda, you are one of the kindest persons I know and your cakes are really special as well. When will you visit us next time? ...And please remember to bring brownies! SandraN, thanks for all the support regarding neighbourhood issues. Eventually we made it! I was wondering about those tiramisù lessons we went through... isn't it time to practice a bit? Sandra dB, thanks for keeping the office always warm either temperature-wise and in spirit. Juju, the master of wall painting (wine-red is your specialty!). Saeed thanks a lot for having daily late lunches with me and endless conversations. Looking forward to meet you some other time. Good luck with the job hunting and for the future! Lukas, thanks a lot for sharing your homemade phosphine. I started by asking about 20 mg and eventually used a gram of it! Without you my chapter 2 would have not been possible. Sometime soon I might need your help to practice back my Italian! Klaas, you can surely inherit part of my glassware when I am gone, but meanwhile I am keeping an eye on you! Andrei, good luck finishing your PhD; Paul, good
job finishing your PhD, you should teach me how you managed to be extremely calm during your defense, or was that your twin brother? Monalisa, good luck with starting your own company, it’s a brilliant idea. The younger HomKat generation. Raoul, so that you know... I will keep borrowing your soxhlet apparatus and eventually I will steal it. Arnout, I like how you are passionate about things, Valentinos, Charles, Kaj, Pim cannot wait for your defense, I have so much material for your paranymphs! Tijmen and Marianne, nice you joined our office. Tiddo, looking forward to your inputs and suggestions. Bin and Shaotao, thanks for your enthusiasm and for sharing some of your chemicals with me.

Now some of the former members; Pawel and Fred, nice parties, Matthias, Yann, sorry for spoiling you surprise birthday party together with Massimo, but it was a great party, Yasemin quietest neighbor ever. Rafa, I did enjoy being your roommates and thanks for introducing me to the cage chemistry. Qiquang, nice cage discussions and could always count on your presence for a working weekend. Danny thanks for all your help with EPR and DFT calculations. Good luck finishing your PostDoc and for what will come after it. Wish you the best of luck. Stefan, man of many cage building blocks, thanks for sharing some with me, Vincent ski pro, we should organize another winter sport event at some point. Sergio and Marc, the smoking postdocs. Thanks to you both for nice and useful discussions. Zhou, Xiaowu, any donation?!?

Some special thanks to the students that I supervised. Stefan, I am extremely satisfied with how you managed your time and the results you have achieved in only few months on a very challenging project. Your learning curve was impressive. Hope at least some of my teachings will be useful in your new PhD adventure. Good luck for that! Sorry your work did not ended up in my thesis; I’ll do my best to finish it up. Alessa, you have learned a great deal in so little time and have done an amazing job. Your project was also very challenging, but you managed to achieve some good results. You got a taste of what doing a PhD means. You definitely have what it takes to get to the end of it. Best of luck for your future! Michiel, although your effort did not go to a good end, we still have learned a lot from your project.

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A special thanks to the AMOLF collaborators, Erik Garnett, Sebastian and Jenny for nice cooperation, discussions and for collecting SEM images. I have learned a lot from you.

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Ad Elisa, sono molto contento di averti conosciuta. Sei una persona stupenda e spero rimarremo buoni amici per lungo tempo.

A (second) special thanks goes to Fenna. Thanks a lot for believing so much in our friendship. I know you started trying already on day 1 and sorry it took so long time for me to open up to you. You always manage to make me feel happy and you always steal a smile from me. I definitely already miss you a lot. Wish we can find a way to stay close friends.

Un grazie di cuore va alla mia famiglia per tutto il supporto ricevuto. Grazie di essermi sempre vicini e di credere in me.

Infine Alessia. Credo una o due frasi scritte qui non siano sufficienti per descrivere tutta la gratitudine nei tuoi confronti. Sono molto fortunato ad averti nella mia vita. Grazie per aiutarmi, sostenermi, stimolarmi a fare meglio, sopportarmi, per essermi sempre vicina e per tutto l’amore che riesci a darmi in ogni singolo momento. Non vedo l’ora di organizzare il nostro futuro e finalmente iniziare il nostro percorso insieme. Ti amo.

Amsterdam, 28 April 2017

Riccardo
About the author
Riccardo was born on the 18\textsuperscript{th} of January 1987 in Como, Italy. Since the high school formation, he has always been interested in food chemistry, cooking science and fishkeeping. Such interests brought him to the chemistry field. After a high school training with a chemist specialization, Riccardo started his academic education at the University of Milano Bicocca at the chemistry department. During the bachelor he participated in the “Erasmus” exchange program and completed a six-month internship at the Royal Institute of Technology (KTH) in Stockholm, Sweden. Under the supervision of Prof. Lars Kloo he investigated the preparation of homo-poly-cationic naked clusters of group 15 elements in unconventional reaction media. During the master period, Riccardo obtained a Cariplo scholarship to perform a ten-month internship at the University of Illinois Urbana-Champaign (UIUC) under the daily supervision of Prof. Thomas B. Rauchfuss. Throughout this period he maturated a strong interest in renewable energies, in particular aimed at transferring the knowledge he gained regarding hydrogenase enzymes to sustainable hydrogen producing devices. In 2012 he graduated from the University of Milano Bicocca under the supervision of Prof. Luca De Gioia and Prof. Thomas B. Rauchfuss, with a thesis on synthesis and characterization of bio-inspired models of the [Fe-Fe]-hydrogenase active site. In the same year, he joined the homogeneous catalysis group (HomKat) lead by Prof. Joost N.H. Reek, at the University of Amsterdam (UVA). His four-year PhD project focused on understanding second coordination sphere effects in synthetic mimics of the [Fe-Fe]-hydrogenase active site. After his PhD, Riccardo will continue to explore his leading interests that have been accompanying him throughout his scientific formation.
List of publications

   “New Tetracobalt Cluster Compounds for Electrocatalytic Proton Reduction: Syntheses, Structures, and Reactivity”

   “Contrasting Protonation Behavior of Diphosphido vs Dithiolato Diiron(I) Carbonyl Complexes”

   “Terminal vs. Bridging Hydrides of Diiron Dithiolates: Protonation of Fe₂(dithiolate)(CO)₂(PMe₃)₄”

   “Reaction of Aryl Diazonium Salts and Diiron(I) Dithiolato Carbonyls: Evidence for Radical Intermediates”

   “Dichloromethane as solvent for the synthesis of polycationic clusters at room temperature; a link to standard organometallic chemistry”
We must not forget that when radium was discovered no one knew that it would prove useful in hospitals.

The work was one of pure science.

And this is a proof that scientific work must not be considered from the point of view of the direct usefulness of it. It must be done for itself, for the beauty of science, and then there is always the chance that a scientific discovery may become, like the radium, a benefit for humanity.

Marie Curie