

The manuscript ja-2016-07987c by Kasoar describes work on Co-Mabiq complexes. They present evidence that they have isolated three oxidation states of these complexes, the parent complex Co(Mabiq)THF, 1, the singly reduced complex Co(Mabiq), 3, and the doubly reduced complex [Co(Mabiq)Na(OET₂)]₂, 2. These systems are of fundamental interest because their HERs now can be studied from a number of entry points. Also with authentic samples of each oxidation state intermediates in the HER reaction can be better identified. Further the authors have characterized the three oxidation states and believe that the ligand plays an important role in the reductions.

The authors introduce the paper with a nod toward development of renewable energy sources and hydrogen evolution reactions as well as the idea that there is a universal mechanism for HER. However, since a number of low overpotential HER solid state catalysts have been developed the importance of homogenous HER catalysts for the development of solar energy conversion devices has become less important. Also no one universal pathway will likely exist for HERs. The mechanism for each catalyst will reflect the thermodynamics and kinetics that are unique to that catalysts. One should not expect that a single pathway will be important for all catalysts and currently it seems that a number of different mechanisms have been established. Also it is probable that the mechanism for a reaction may differ for an electrode driven HERs of homogenous catalysts as opposed to a homogeneously driven HER.

The idea that there exists multiply pathways for HER catalysts has been proposed and a number of different pathways have been suggested. A reduced metal complex can add a proton to either the metal center or possibly to a ligand and then the protonated complex will react with another proton, or with another protonated complex, or be further reduced and then react to produce hydrogen. These various pathways have been discussed in the literature. In a number of systems there is experimental and theoretical evidence that the Co^{III}dmgH reduction potential is close to or more positive than the Co^{III}/I reduction potential and thus making the HER pathway via the Co^{II}H species viable. The importance of the present communication is that it looks to validating a pathway that involves direct ligand involvement in the protonation, not invalidating other pathways.

This manuscript reports the isolation of three oxidation states of a Co(Mabiq) complex. While the manuscript initially notates them as a Co^{II}, Co^I and Co⁰ they go on to suggest that it is likely that they all (or mostly) Co^{II} centers and that the ligands play a noninnocent role. These complexes are interesting and the exact mechanism of their HER is of importance. However, the current manuscript does not address this aspect. Rather it characterized the cobalt products on addition of a proton source. There is no analysis of H₂ production, the kinetics of the reaction, or the mechanism. The paper does suggest that protonation of 2, the doubly reduced product of Co(Mabiq)THF, adds protons to the ligand rather than the metal center. The manuscript does not address the thermodynamics of the overall HER process.

I think it would be better if the authors wait to publish a more complete description of the mechanism and kinetics of the HER of the Co-Mabiq complexes. Also I don't think that the novelty of the work makes a compelling case for publication in JACS. Rather a more specialized journal would seem appropriate.

Small comments:

- 1) The numbering scheme is somewhat confusing since the numbers are not in order of the reduction of the complexes, while 1 is the parent 2 is the doubly reduced and 3 is the singly reduced complex.
- 2) The authors often refer to the complexes as the Co^1 and Co^0 complex however they suggest that none have a Co^0 center and that maybe none are really even Co^1 . It might be less confusing to refer to them as the singly and doubly reduced complex.
- 3) Line 34 page 3 says a reaction pathway cleanly converts cpd 2 to cpd 3. What is meant is not clear since in the next sentence they say that ~40% of 2 converts to something else.
- 4) Scheme 2 is mislabeled as Scheme 1.