Synthesis, Structure and Reactivity of Ni Site Models of [NiFeSe] Hydrogenases

Electronic Supporting Information (ESI)

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1. Supporting Table

Table S1. Hydrogen production activity and faradaic efficiency of Ni modified FTO electrodes with a geometric surface area of 1.6 cm² after 10 h controlled potential electrolysis in pH 7 phosphate buffered water (0.1 M) at an applied potential of -0.9 V vs. NHE. The electrodes were modified with Ni by electrodeposition of $(n-Bu_4N)[Ni(L^E)(Mes^{E'})]$ (1mM in acetonitrile, 0.1 M $n-Bu_4NBF_4$) at -1.33 V vs. NHE for 0.5 h at room temperature.

Molecular Ni Precursor	H_2 / $\mu \mathrm{mol}$	Faradaic Efficiency / %
$(n-\mathrm{Bu}_4\mathrm{N})[\mathrm{Ni}(\mathrm{L}^{\mathrm{Se}})(\mathrm{Mes}^{\mathrm{S}})$	55 ± 20	71 ± 2
(<i>n</i> -Bu ₄ N)[Ni(L ^{Se})(Mes ^{Se})]	41 ± 9	63 ± 2
$(n-\mathrm{Bu}_4\mathrm{N})[\mathrm{Ni}(\mathrm{L}^{\mathrm{S}})(\mathrm{Mes}^{\mathrm{Se}})]$	9 ± 2	67 ± 5
(<i>n</i> -Bu ₄ N)[Ni(L ^S)(Mes ^S)]	22 ± 1	64 ± 9

Electronic Supplementary Material (ESI) for Dalton Transactions This journal is $\ensuremath{\mathbb{C}}$ The Royal Society of Chemistry 2013

2. Supporting Figures

2.1. Characterisation of Compounds



Figure S1. ¹H NMR spectrum of $({}^{c}L^{Se}-H')_{2}$ in CD₂Cl₂ ('as recorded' before correcting chemical shift against solvent peak).



Figure S2. ¹H NMR spectrum of 'L^{Se'}-H₂ in CDCl₃ ('as recorded' before correcting chemical shift against solvent peak).



Figure S3. ¹H NMR spectrum of $(n-Bu_4N)[Ni(L^{Se})(Mes^S)]$ in THF- d_8 ('as recorded' before correcting chemical shift against solvent peak).



Figure S4. ¹H NMR spectrum of $(n-Bu_4N)[Ni(L^{Se})(Mes^{Se})]$ in THF- d_8 ('as recorded' before correcting chemical shift against solvent peak).



Figure S5. ¹H NMR spectrum of $(n-Bu_4N)[Ni(L^S)(Mes^{Se})]$ in THF- d_8 ('as recorded' before correcting chemical shift against solvent peak).



Figure S6. ¹H NMR spectrum of $(n-Bu_4N)[Ni(L^S)(Mes^S)]$ in THF- d_8 ('as recorded' before correcting chemical shift against solvent peak).



Figure S7. ¹H NMR spectrum of $(PPh_4)[Ni(L^S)(Mes^{Se})]$ in CD_2Cl_2 ('as recorded' before correcting chemical shift against solvent peak).



Figure S8. ¹H NMR spectrum of $(PPh_4)[Ni(L^S)(Mes^S)]$ in CD_2Cl_2 ('as recorded' before correcting chemical shift against solvent peak).



Figure S9. Mass spectrum of ('L^{Se,}-H)₂ in CHCl₃.



Figure S10. Mass spectrum of 'L^{Se}'-H₂ in CHCl₃.



Figure S11. Top: Mass spectra of $(n-Bu_4N)[Ni(L^{Se})(Mes^S)]$ in CH_2Cl_2 (+ive and -ive mode; left and right, respectively). Bottom: Predicted spectrum of the anion.





Figure S12. Top: Mass spectrum of $(n-Bu_4N)[Ni(L^{Se})(Mes^{Se})]$ in CH_2Cl_2 (+ive and -ive mode; left and right, respectively). Bottom: Predicted spectrum of the anion.



Figure S13. Top: Mass spectrum of $(n-Bu_4N)[Ni(L^S)(Mes^{Se})]$ in CH_2Cl_2 (+ive and –ive mode; left and right, respectively). Bottom: Predicted spectrum of the anion.



Figure S14. Top: Mass spectrum of $(n-Bu_4N)[Ni(L^S)(Mes^S)]$ in CH_2Cl_2 (+ive and –ive mode; left and right, respectively). Bottom: Predicted spectrum of the anion.



Figure S15. Mass spectrum of $(PPh_4)[Ni(L^S)(Mes^{Se})]$ in CH_2Cl_2 (+ive and -ive mode; left and right, respectively).



Figure S16. Mass spectrum of $(PPh_4)[Ni(L^S)(Mes^S)]$ in CH_2Cl_2 (+ive and -ive mode; left and right, respectively).



Fig S17. ATR-IR spectrum of $[Ni(L^{Se})_n]$.

2.2. Characterisation of Oxidation Products



Figure S18. ATR-IR spectrum of $[Ni(L^S)]_n$ isolated from the oxidation of PPh₄ $[Ni(L^S)(Mes^{Se})]$.



Figure S19. ¹H NMR spectrum of dimesitylene diselenide isolated from the oxidation of $(PPh_4)[Ni(L^S)(Mes^{Se})]$ in CDCl₃ ('as recorded' before correcting chemical shift against solvent peak).



Figure S20. EI Mass spectrum of dimesitylene diselenide in $CHCl_3$ isolated from the oxidation of $(PPh_4)[Ni(L^S)(Mes^{Se})]$.



Figure S21. ¹H NMR spectrum of dimesitylene disulfide isolated from the oxidation of (PPh₄)[Ni(L^S)(Mes^S)] in CDCl₃ ('as recorded' before correcting chemical shift against solvent peak).



Figure S22. ¹H NMR spectrum in CD_2Cl_2 of $(PPh_4)[Ni(L^S)(Mes^{Se})]$ (left column) and $(PPh_4)[Ni(L^S)(Mes^S)]$ (right column) at different time intervals following exposure to atmospheric oxygen (*starting material, [†]product).

2.3. Characterisation of HBF₄ Reaction Products



Figure S23. ¹H NMR spectrum of mesitylene selenol in CDCl₃ isolated from the protonation of $(n-NBu_4)[Ni(L^S)(Mes^{Se})]$ ('as recorded' before correcting chemical shift against solvent peak).



Figure S24. ¹H NMR spectrum of mesitylene thiol in CDCl₃ isolated from the protonation of $(PPh_4)[Ni(L^S)(Mes^S)]$ with HBF₄ ('as recorded' before correcting chemical shift against solvent peak).

2.4. Electrochemical and Deposition Studies



Figure S25. Cyclic voltammograms of $(n-Bu_4N)[Ni(L^E)(Mes^{E'})]$ (1 mM) in an acetonitrile solution containing $n-Bu_4NBF_4$ (0.1 M) at a scan rate 100 mV s⁻¹.



Figure S26. Cyclic voltammograms of $(n-Bu_4N)[Ni(L^{Se})(Mes^S)]$ (1 mM) at 100 mV s⁻¹ in the presence of $n-Bu_4NBF_4$ (0.1 M) in acetonitrile (black), dimethyl formamide (red) and dichloromethane (blue).



Figure S27. Cyclic voltammograms of $(n-Bu_4N)[Ni(L^{Se})(Mes^{Se})]$ (top), $(n-Bu_4N)[Ni(L^{S})(Mes^{Se})]$ (middle) and $(n-Bu_4N)[Ni(L^{S})(Mes^{S})]$ (bottom) in an acetonitrile solution (1 mM) containing $n-Bu_4NBF_4$ (0.1 M) at a scan rate of 100 mV s⁻¹ with 0 mM (black), 1 mM (red), 3 mM (blue), 5 mM (pink) and 10 mM (green) Et₃NHCl (second scan of consecutive scanning cycles shown in all cases).



Figure S28. Left: Plot of first derivative of the catalytic wave of the reduction of protons in NEt₃HCl (10 mM) in the presence of $(n-Bu_4N)[Ni(L^{Se})(Mes^S)]$ (1mM), $E_{1/2} = E_{max} + 0.015$ (V. Fourmond, P.-A. Jacques, M. Fontecave and V. Artero, *Inorg. Chem.*, 2010, **49**, 10338–10347). Right: Plot of catalytic current (i_{cat}) as a function of Et₃NHCl concentration. Half wave potential was calculated at an acid concentration of 10 mM where the relationship between catalytic current and acid concentration is linear.



Figure S29. $(n-Bu_4N)[Ni(L^{Se})(Mes^S)]$ (1 mM) in acetonitrile (10 mM Et₃NHCl, 0.1 M *n*-Bu₄NBF₄) at a glassy carbon disk working electrode (black trace). The glassy carbon electrode was subsequently rinsed with acetonitrile and transferred to a fresh Ni-free acetonitrile solution (10 mM Et₃NHCl, 0.1 M *n*-Bu₄NBF₄) (blue trace). A control experiment with a polished glassy carbon electrode in Ni-free acetonitrile (10 mM Et₃NHCl, 0.1 M *n*-Bu₄NBF₄) is shown as the red trace.



Figure S30. Electronic absorption spectrum of $(n-Bu_4N)[Ni(L^E)(Mes^{E'})]$ (0.1 mM) in MeCN in the presence (black) and absence (red) of Et₃NHCl (1 mM).



Figure S31. (a) SEM of FTO electrode (1.6 cm² surface area) after electrodeposition of $(n-NBu_4N)[Ni(L^{Se})(Mes^S)]$ (1 mM, 5 mL in acetonitrile, 0.1 M $n-Bu_4NBF_4$, applied potential of -1.33 V vs. NHE for 0.5 h). (b) Full frame EDX of spectrum of (a).



Figure S32. Electrocatalytic H₂ production during CPE with Ni modified FTO-electrodes (geometric surface area of 1.6 cm²) over 10 h in pH 7 phosphate buffered water (0.1 M) at -0.9 V vs. NHE. The electrodes were modified with Ni by electrodeposition of $(n-Bu_4N)[Ni(L^E)(Mes^{E'})]$ (1 mM in acetonitrile, 0.1 M *n*-Bu₄NBF₄, 10 mM Et₄NHCl) at -1.33 V vs. NHE for 0.5 h. Hydrogen production activity of a platinum foil with the same surface area is also shown for comparison.

3. Letter written by Dr. John Davies about refinement of X-ray crystal structures.

These four structures contain a total of seven tetra-*n*-butylammonium cations in their asymmetric units. In each case the cation is poorly resolved. This is because, despite strenuous efforts (multiple datasets from different crystals) to obtain good data, the crystal quality was poor and so the diffraction data is poor. If anisotropic displacement parameters are assigned to the carbon atoms of these cations, no amount of fussing with fancy *SHELXL* commands will produce thermal parameters, which are at all believable. Instead, the carbon atoms of these cations were each assigned one of four common isotropic displacement parameters for the refinement process. So, instead of the 96 (or 192) least squares variables which would be needed for one (or two) cations if anisotropic displacement parameters were used for all atoms, this refinement process uses only *four* (& note: three of the structures in this paper contain two cations in their asymmetric unit). In addition, weak bond length constraints were applied to keep the geometry of these chains chemically sensible (one extra least squares variable per structure).



Figure S33. Left: a cation (from ER1212) refined using 4 common isotropic displacement parameters for the carbon atoms. Right: the same cation refined using individual anisotropic displacement parameters (96 parameters) for each carbon atom

The quality of the data did vary somewhat between the four structures. Here is a typical frame from ER1212 \dots



Figure S34. Typical frame from ER122. The highest angle diffraction spots in this frame are at ca $2\theta(Mo) = 20^{\circ}$. There was effectively no measurable data above this limit and so the resolution of the whole experiment is poor

The fact that, in each of the four structures, the final four refined isotropic displacement parameters increase along each *n*-butyl chain, outwards from the central nitrogen atom, does make sense if one assumes (very reasonably) that these chains are waggling about. The same effect is certainly visible if one assigns anisotropic displacement parameters instead - but is there really any more information in these 96 numbers? Particularly if one attempts to constrain them with extra SHELXL commands no matter whether 'soft', 'gentle' or 'hard' (adjectives which I think are best set aside for soap commercials)? Frankly I doubt it. The sad fact which we must all face is that our crystallographic literature is stuffed full of anisotropic displacement parameters which mean absolutely nothing at all and which (quite rightly) receive no attention from anybody. Rather than urge authors to fiddle around with funny anisotropic displacement parameters in a forlorn attempt to make them look more 'respectable', many referees would do us all a service if they encouraged intelligent and more frequent use of common isotropic displacement parameters. At the same time, many authors should stop urging their X-ray technical staff to use anisotropic displacement parameters no matter what, for fear that their papers may otherwise be rejected by their crystallographic referees. The whole thing is a vicious spiral and someone somewhere somehow needs to put a stop to it. I suggest we begin right here, with this paper.

Rather than focusing entirely on displacement parameters in an attempt to determine the effectiveness of the refinement strategy adopted for these four structures, it is instructive to compare the R(merge) of each dataset with the 'final R1' value. Here are the numbers (final R1 values in parentheses): 0.062(0.071); 0.058(0.076); 0.077(0.045); 0.134(0.107). Two of the R1 values are slightly higher than their R(merge) values and two are lower. These numbers indicate that the accuracy of each final refinement model here is very harmoniously matched to the accuracy of its diffraction data.

In the refinement of these four structures it would actually have been much easier to go with the referee's suggestions, assigning anisotropic displacement parameters and adding a few 'soft' and 'gentle' constraints (whatever they may be). Instead, we have worked much harder to refine these four structures in the way we have described, paying very careful attention to the assignment of the required 'free-variables' and 'DFIX' instructions in the *SHELXL* command file. The final result is that the seven tetra-*n*-butylammonium cations in these four structures have been refined very satisfactorily indeed with only 16 common isotropic displacement parameters. By 'very satisfactorily' we mean (a) that the accuracy of the final refinement models (indicated by the final R1 values) is approximately the same as the accuracy of the datasets (indicated by the R(merge) values) and (b) the resulting isotropic displacement parameters really do look physically reasonable (similar in each case, indicating that all seven cations are 'waggling' about in a similar fashion).

For every tetra-*n*-butylammonium cation in these four structures, the geometric constraints for the refinement were the same, accomplished with one extra least squares parameter 'd1'. All distances between adjacent atoms were constrained to be d1(0.05)A and all distances between atoms once-removed were constrained to be 1.633*d1Å. Effectively, these two constraints together ensure that all N-C and C-C distances in each chain will be d1(0.05)Å and all angles N-C-C and C-C-C will be approximately tetrahedral.

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