New synthetic Mo/Fe/S clusters: Potential biological relevance

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In pursuit of new synthetic analogues of the FeMo-cofactor of the nitrogenase enzyme, we were able to obtain a new class of Mo/Fe/S clusters with the $Mo_2Fe_6S_8$ core, as derivatives of the known $(Cl_4\text{-cat})_2Mo_2Fe_6S_8(PPr_3)_6$ (**I**) fused double cubane. The new clusters have been obtained by substitution reactions of the PPr_3 ligands with Cl^-, BH_4^- and N_3^-. By careful control of the conditions of these reactions, the clusters $[(Cl_4\text{-cat})(PPr_3)MoFe_3S_4(BH_4)_2]_2(Bu_4N)_4$ (**II**), $[(Cl_4\text{-cat})(PPr_3)MoFe_3S_4(PPr_3)(BH_4)]_2(Bu_4N)_2$ (**III**), $[(Cl_4\text{-cat})(PPr_3)MoFe_3S_4(N_3)_2]_2(Bu_4N)_4$ (**IV**), $[(Cl_4\text{-cat})(PPr_3)MoFe_3S_4(PPr_3)(N_3)]_2(Bu_4N)_2$ (**V**), $[(Cl_4\text{-cat})(PPr_3)MoFe_3S_4Cl_2]_2(Et_4N)_4$ (**VI**) have been obtained and structurally characterized.

The study of their electrochemistry shows that the reduction potentials for the derivatives of **I** are shifted to more positive values as compared to those of **I** suggesting a stabilization of the reduced clusters by the anionic ligands, BH_4^- and N_3^-. Using ^1H NMR spectroscopy the lability of the BH_4^- ligand in **II** in coordinating solvents has been explored as well as its hydridic character apparent in its reactivity towards proton-sources such as MeOH or PhOH.

Furthermore these clusters might provide a synthetic pathway to the formation of compounds with potential relevance to the nitrogenase MoFe-cofactor. Preliminary results towards this objective will be presented.