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Preface

Metallosulfur clusters in diverse enzymes provide the active sites which catalyse a range of extraordinary reactions, for example, nitrogen fixation by the nitrogenases, inter-conversion of CO_2 and CO by the CO dehydrogenases, methylation of CO by the acetyl CoA synthetases and, the focus of this issue of Coordination Chemistry Reviews, inter-conversion of dihydrogen/protons + electrons by the hydrogenases. Why extraordinary? . . . Because with current technology these same economically important reactions demand precious metal catalysts or high temperatures and pressures to proceed at reasonable rates. The enzymes have somewhat more in common: we do not really know the detail of how any work at the molecular level. Nitrogenase is perhaps the paradigm, every new spectroscopic, theoretical and physical technique that comes along has been thrown at the problem, but we are still rather unclear as to where dinitrogen binds, why hydrogen is concomitantly evolved, the oxidation states of the metals in the resting and turnover states and so forth. The metallosulfur active sites of the hydrogenases promise to be somewhat more amenable and, in terms of the social, economic and industrial impacts of the hydrogen economy, equally significant. The realisation of highly active low-temperature hydrogen activation catalysts based on cheap, abundant chemicals constitutes one of the "breakthrough advances" needed to realise this technology shift. Faced with a different set of imperatives hydrogenases evolved some 3 billion years ago. Much of the research effort devoted into unravelling the hydrogenase puzzle, and the funding devoted thereto, is justified on the basis of the connection between the technological problem and the evolutionary solution. While such an advance may directly, or indirectly, result from this research, the elucidation of the details of the chemistry of the hydrogenases represents an important goal in its own right.

The detection of metal cyano and carbonyl complexes at the active sites of the hydrogenases by infrared spectroscopy and the elucidation of the crystal structures in the mid to late 1990s has facilitated the broadening of the research front to include card-carrying coordination chemists. The remarkable structures of the active sites of both the [NiFe] and [FeFe] hydrogenases has led to the productive re-examination and development of aspects of the chemistry of iron carbonyl and iron carbonyl/cyanide chemistry. This, in turn, has yielded abiological compounds that are structural and functional models of the active site. The prospects for the translation of these advances into useful materials would seem to be bright. Against this backdrop there are equally impressive advances in the understanding of the enzymes and the development of protocols that facilitate application [NiFe]-hydrogenases as electrocatalysts in prototype fuel cells.

At this time there is a particularly fruitful dialogue between practitioners in fields as disparate as structural biology, spectroscopy and electrochemistry where a key central theme is coordination chemistry – and we can look forward to new structural and spectroscopic knowledge of what was the 'metal free' and what is now the 'cluster-free' Fe-hydrogenase. This special issue of Coordination Chemistry Reviews brings together contributions that reflect the multidisciplinary nature of the field, the recent significant advances and gives a sense of the challenges that remain unresolved. We thank the contributors to this issue for their efforts and hope that the readers of these articles will find them useful in their endeavours to advance this and other areas of science.

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