7: Ferrodoxins, Hydrogenases, and Nitrogenases - Metal-Sulfide Proteins

Transition-metal/sulfide sites, especially those containing iron, are present in all forms of life and are found at the active centers of a wide variety of redox and catalytic proteins. These proteins include simple soluble electron-transfer agents (the ferredoxins), membrane-bound components of electron-transfer chains, and some of the most complex metalloenzymes, such as nitrogenase, hydrogenase, and xanthine oxidase. In this chapter we first review the chemistry of the Fe-S sites that occur in relatively simple rubredoxins and ferredoxins, and make note of the ubiquity of these sites in other metalloenzymes. We use these relatively simple systems to show the usefulness of spectroscopy and model-system studies for deducing bioinorganic structure and reactivity. We then direct our attention to the hydrogenase and nitrogenase enzyme systems, both of which use transition-metalsulfur clusters to activate and evolve molecular hydrogen.

I. Iron-sulfur Proteins and Models

A. Rubredoxin: A Singe-Fe Tetrathiolate Protein

B. Rubredoxin Model Systems

C. Fe_2S_2 Ferredoxins

D. Rieske Centers

E. Fe_2S_2 Models

F. Fe_4S_4 Ferredoxins (including HiPIPs)

G. Fe_4S_4 Models

H. Core Extrusion/Cluster Displacement Reactions

I. Fe_3S_4 Centers

J. Fe_3 Model Systems

K. Fe-S Chemistry: Comments and New Structures

L. Detection of Fe-S Sites

M. Redox Behavior

II. Multisite Redox Enzymes

A. Hydrogenase and Nitrogenase

B. Hydrogenases

1. Physiological Significance
2. Dihydrogen: The Molecule
3. Iron Hydrogenases
4. Nickel-iron Hydrogenases
5. Insights from Inorganic Chemistry

C. Nitrogenases

1. The Scope of Biological Nitrogen Fixation
2. Dinitrogen: The Molecule and Its Reduced Intermediates
3. The Dominant Hypothesis for Molybdenum Nitrogenase[239,240,242,243]
4. Protein Purity and Active Sites
5. FeMoco
6. The P-clusters
7. EPR, ENDOR, and ESEEM studies
8. Mössbauer Studies
9. X-ray Absorption Studies

10. Substrate Reactions
11. The Role of ATP

D. The Alternative Nitrogenases

1. Vanadium Nitrogenase
2. The All-iron Nirogenase[322]
3. Model Systems

E. N_2 and Related Complexes

F. Insights from Relevant Inorganic Reactivity

III. Report on the Nitrogenase Crystal Structure[378-381]

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Contributors and Attributions

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