on subjects where one is more ignorant. As a reference source for the library of any laboratory working in the field of catalysis, this would be hard to fault. It could be safely taken as a starting point for new or experienced researchers wanting a good digest of a specific field.

The five volumes are beautifully produced, with very clear diagrams and a reasonably good index. Overall the book can be recommended.

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Structure and Bonding—Metal Sites in Proteins and Models. H.A.O. Hill, P.J. Sadler, A.J. Thompson (Eds.), Springer, New York, NY, 1997 (vols. 88 and 89), 1998 (vol. 90).
Vol. 88, *Iron Centres* 225 pages, US$129, ISBN 3-540-62870-3.
Vol. 89 *Phosphatases, Lewis acids and Vanadium* 215 pages, US$129, ISBN 3-540-62874-6.
Vol. 90 *Redox Centres* 209 pages, US$129, ISBN 3-540-62888-6.

This three-part special series of *Structure and Bonding* has topics on 'Metal Sites in Proteins and Models' as it's focus, a field which has undergone vigorous expansion and development in recent years. The three-dimensional structures of many of the proteins and enzymes of interest have been determined at high resolution, opening the way for molecular engineering of metal binding sites. Additionally, the application of an array of techniques including NMR, X-ray absorption, EPR and MCD spectroscopies, coupled with the development of biomimetic chemical and structural models, has fuelled this expansion. In these volumes recent advances in inorganic biochemistry are reviewed by leading scientists of international standing. They bring together information that it is hoped will stimulate researchers attempting to understand the relationships between the chemistry of metals and their involvement in a diverse range of life processes. In broad outline, these reviews address different aspects about how a protein environment controls the properties of metal sites and how do they compare with those found in small coordination complexes?

Commensurate with the diversity of its biological roles, vol. 88 of this series is devoted to *iron-dependent systems and processes*. These include contributions on several heme-containing enzymes, the uptake of Fe(II) storage as Fe(III) in bacterioferritin, the sequestration of Fe(III) by transferrin, radical chemistry in deoxyribonucleotide synthesis and models for biomineralisation.

In an aerobic aqueous environment at neutral pH, Fe(III) is present predominantly as insoluble oxyhydroxides, yet iron is intimately involved in many biological processes. Powell discusses how the speciation of iron may be controlled in Nature using a templating matrix to control biomineralisation. A range of structurally characterised iron oxyhydroxide clusters are considered as models for the core of loaded ferritins, large protein assemblies that have a role in providing a cage for the intracellular storage of Fe(III) species. Structural, spectroscopic and chemical studies of the metal centres of bacterioferritin, a cytochrome b_5 containing member of the ferritin family, are discussed by Brun et al. The oxidative uptake of Fe(II) by bacterioferritin appears to involve a dinuclear metal centre that has structural similarities to the di-Fe(II) centre of the R2 protein of ribonucleotide reductase. Roles of these metal centres in iron uptake and released are critically reviewed.

Ribonucleotide reductases are essential to living cells since they provide precursors for DNA synthesis. Three unique classes of this enzyme that differ in composition and cofactor requirements (a Fe(III) di-iron-oxo site, an FeS cluster or a Mn site depending on the source of the material) all use radical chemistry to activate their substrates. Sjöberg describes structural, spectroscopic and directed mutagenic studies highlighting mechanistic studies of these systems.

Two chapters on heme-containing systems, one on $P450_{CAM}$ by Wong et al., and the other on 'why heme is the most versatile redox centre in biology' by Chapman et al., are highly informative, and nicely illustrate the impact which crystal structures can make on an area of research. The review on $P450_{CAM}$ focuses on the use of protein engineering to change the specificity of the enzyme by redesigning the active site to use high-energy oxo-iron chemistry for new biotechnological applications. The title of the review of Chapman et al. is deliberately provocative, but the carefully chosen examples and the subsequent discussion of the many redox functions performed by heme in biology, fully support the title of this contribution.

Transferrins are Fe(III) binding proteins that function in iron transport in serum and have antimicrobial activity. Sun et al. present a detailed discussion of methods for studying differences between the two metal binding sites and the determination of metal binding constants. They present a predictive rationalisation of metal binding properties of transferrin, based on a correlation with ion acidity. This appears to be applicable to carbonic anhydrase and carboxypeptidase enzymes that have 'entatic state' metal binding sites in contrast to the highly flexible metal binding site of transferrin.

Phosphatases, *Lewis acids and Vanadium* form the backbone of vol. 89 of this series. The control of cellular metabolism in many cases is archived by the reversible phosphorylation of key enzymes by protein kinases and their dephosphorylation catalysed by phosphatases. A comprehensive overview of structural and kinetic data on the role of metal ions (Zn, Mg, Ni, Mn, Fe) in providing Lewis acid coordination during the enzymic hydrolysis of phosphate monoesters, is presented by Gani and Wilkie. Following an introduction to the non-enzymic and enzymic paths of phosphate ester hydrolisis, the structure and mechanism of several enzymes are considered leading to the view for a common mechanism operating. This theme is developed in more detail for the purple acid phosphatases by Kalbunde and Krebs, who focus on the structure, spectroscopic properties, and a proposed mechanism of these enzymes. The colour of these phosphatases is associated with a charge transfer band arising from the ligation of a tyrosine residue to a ferric ion. These enzymes contain a dinuclear metal centre, di-iron in the mammalian enzymes, and a heterodinuclear Fe(III), Zn(II) in the plant enzyme. The di-iron centre of the mammalian enzyme is similar to that of ribonucleotide reductase, an enzyme reviewed in vol. 88 of this series.

Zinc is an essential metal in biology, and has been shown to have catalytic, structural and co-catalytic roles in a range of enzymes. Its ability to accommodate a broad range of geometries and coordination numbers, in addition to its Lewis acid properties, readily accounts for this versatility. The contribution by Auld summarises these structural elements and then focuses on the Zn-containing proteases. The application of X-ray absorption spectroscopy to reveal the structure, and using time-resolved EXAFS, the reactivity of carboxypeptidase, is discussed in some detail. Recently developed mononuclear zinc(II) complexes as functional models for carbonic anhydrase, alkaline phosphatase and alcohol dehydrogenase are reviewed by Kimura et al. The importance of Lewis acidity and the basicity of Zn(II)-bound hydroxide are emphasised in the context of model chemistry of these enzymes, in addition to a summary of recent progress in protein engineering of catalytic sites.

Vanadium has been shown to have distinct biological roles in two classes of enzymes, V-dependent haloperoxidases and nitrogenases, and in addition, vanadate has insulin-mimetic properties. Although vanadium is accumulated to high concentrations as tunichrome compounds in some marine organisms and as amavadin in the mushroom *Amanita muscaria*, the biological function of these compounds is uncertain. Slebdonick et al. review the coordination chemistry of vanadium and the reactivity of model compounds of these systems and in insulin-mimetic properties. The utility of vanadate interactions with ATPases, where vanadate induces photocleavage of the polypeptide at the nucleotide binding site, is also reviewed. Model compounds (both spectroscopic and functional) for the V-dependent haloperoxidases, and to a more limited extent V-nitrogenases, are authoritatively discussed. Butler and Baldwin focus in more detail on the structure reactivity and kinetics of V-dependent bromoperoxidases and chloroperoxidases (the crystal structure of the latter is described by Messerschmidt in vol. 90). Functional mimics of V-haloperoxidase, including peroxo-complexes of V(V) and other transition metal ions useful in testing mechanistic hypotheses, are also described in depth.

Vol. 90 is focused on *redox centres in proteins* and their ability to bring about electron transfer reactions in a controlled manner. Metals from the three transition metal series are discussed: V, Mn, Fe, Ni and Cu from the first, Mo from the second, and W from the third.

Mo and W are found associated with several enzymes involved in the metabolism of nitrogen, sulfur and carbon. Except for nitrogenase, where Mo is present in FeSMo(or V) clusters, Mo and W enzymes contain a mononuclear metal centre coordinated by the dithiolene sulphur atoms of a pterin. Mo enzymes are classified into the xanthine oxidase family, sulphite oxidase and assimilatory nitrate reductase family, and the dimethylsulphoxide reductase family. A number of crystal structures of these enzymes have been solved recently, and here Romao and Huber describe the structure of the aldehyde oxido-reductase of *Desulphvibrio gigas*, a typical member of the xanthine oxidase family. Spectroscopic, kinetic and studies on model compounds are drawn together to provide insight on the mechanism of action of the enzyme. The chemistry and biological importance of W in several enzymes is comprehensively presented by Hagen and Arendsen. They stress that spectroscopic studies of W centres in proteins is in its infancy, but fortunately, a crystal structure of the W-containing aldehyde oxidase of *Pyrococcus furiosus* has been determined, and shows that the binding site is a dimer of two pterins, in which both dithiolene groups coordinate to the W atom. Spectroscopic data for the W in the tungstopterin, the 4Fe–4S centre and the 'enigmatic' nature of the intersubunit metallocentre are critically reviewed against the background of the crystal structure.

Blue copper centres in cupredoxins and the blue copper oxidases are described by Messerschmidt. The structures of these centres determined by X-ray crystallography, and the insight provided by the study of mutant proteins engineered to modulate spectroscopic properties, demonstrates the power of such an interdisciplinary approach. These studies have enabled a classification of such sites dependent on their detailed coordination geometry. More complex geometries exemplified by the purple dinuclear copper site of cytochrome c oxidase and nitrous oxide reductase, and the trinuclear sites of ascorbate oxidase and the internal electron transfer pathways are also discussed. This contribution ends with a description of the structure of the first vanadium containing enzyme to be solved, a chloroperoxidase for which the geometry of the catalytic V centre is revealed. The wider chemistry and biochemistry of the fairly recent addition of V to the realm of biologically relevant metals are to be found in vol. 89.

A critical evaluation of the available structural data (mostly provided by EPR and X-ray absorption spectroscopy) to assess possible models for the mixed valence Mn-containing centre in the oxygen-evolving complex responsible for green plant photosynthesis is given by Penner-Hahn. The structural and redox properties of synthetic FeS clusters are discussed by Capozzi et al. before they consider parameters important in fine-tuning redox potentials by the protein environment. This is achieved by comparison of the crystal structures of the FeS proteins (which exhibit a wide range of midpoint potentials) with NMR and other spectroscopic data, to define electron distribution within the cluster. Nickel/iron hydrogenases have shown some very surprising results from IR and EPR spectroscopies, together with crystallographic studies. Frey describes the model for the *D. gigas* enzyme where the three FeS centres (two 4Fe–4S and one 3Fe–4S) are aligned and separated by ≈ 12 Å. The Ni centre is bimetallic containing one Ni and one Fe atom separated by 2.8 Å with one CO and two CN ligands to the Fe atom.

I highly recommend this series of very readable and stimulating reviews. They provide a valuable resource for chemists and biochemists interested in (or wishing to find out more about) the roles played by metals in biological processes. The wide range of topics covered, and organisation of the series gives added value to many of the individual contributions, should result in effective cross-discipline intellectual stimulation. The series is well produced and cross-referenced within the articles. Particularly important, abbreviations and acronyms are defined and accessible (except for the single letter code used for amino acids), a surprising omission given the catholic nature of the projected readership, and the abundance of amino acid sequence comparisons and protein structures using this notation. A small quibble for a useful series covering a wide field of information.

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Metal Catalyzed Cross-Coupling Reactions, F. Diederich and P.J. Stang (eds.), Wiley–VCH, Chichester, 1998, pp. 571 + xxi, £ 85, ISBN 3-527-29421-X

As the editors point out in their forward, methodology for the formation of carbon–carbon bonds between sp^2 and sp centres has advanced dramatically over the last 25 years. In the most widely used version of the genre, an organometallic nucleophile is coupled with an aryl, alkenyl, alkynyl, propargyl, benzyl or allyl halide in the presence of a complex of nickel, palladium or copper. This volume, however, will take the reader far beyond these prototypes.

The first chapter, by Negishi and Liu, reviews palladium and nickel catalyzed couplings of organometallics of zinc, magnesium, aluminium and zirconium. The authors make some useful generalisations about the relative reactivities of various systems. They describe classic examples, recent work with tosylates, complex natural product syntheses, enantioselective versions of the reaction, and tandem processes. The chapter concludes with a section detailing representative experimental procedures—as does each of the other chapters. The examples are well-chosen and concisely described, but I wonder if a conscientious experimentalist would really use this rather than go back to read the original paper.

Next Suzuki describes coupling reactions of organoboron compounds with organic halides, these being almost invariably catalyzed by palladium complexes. The synthesis of useful organoboron compounds is discussed in some detail, and carbonylation and reactions with triflates more briefly. The Heck reaction is reviewed by Bräse and de Meijere, with a comprehensive and thorough discussion of all the many variants of conditions, substitution patterns, leaving groups and additives which have found favour over the last 25 years. Cascade reactions, multiple couplings and enantioselective processes are all well discussed. Although all the chapters are well-referenced, this one is particularly thorough.

The volume is dedicated to the late John Stille, and Mitchell reviews the Stille coupling of organotin compounds. This is a thorough chapter with most of the references to 1990s work. Sonogashira describes the somewhat less common cross-couplings involving sp-carbon atoms. Almost all of these involve an alkenyl or aryl halide. Link and Overman discuss the use of the Heck reaction in natural product chemistry, focusing especially on ring synthesis and tandem processes. In Ch. 7, Marek and Normant review carbometallation reactions of alkynes, allenes, enynes and alkenes, with particular emphasis on intramolecular processes. Bäckvall is an excellent choice to review 1,4-additions to dienes, catalyzed by palladium complexes, a field in which he is a world leader. Knochel describes reactions of organozinc reagents and Hiyama considers