5 SUMMARY

This review has emphasised the importance of precise stereochemical data in the determination of the structural basis of metal-ion function and reactivity in proteins and enzymes. The resolving power of protein X-ray crystallography has been discussed in general to indicate the origins of the approximate stereochemical data characteristic of protein structures at present, in comparison to the results of small-molecule X-ray crystallography. Possible directions through which improved stereochemical detail of proteins may be obtained in the future have been briefly discussed, especially with respect to their metal–ligand co-ordination centres.

A comparison of stereochemical origins of three categories of metal–protein interaction has been made on the basis of high-resolution X-ray diffraction studies of a number of proteins and enzymes. With reference to metal–ligand co-ordination centres in proteins, detailed correlations of molecular structure, stereochemistry and electronic structure in assessing the biological role of metal-ion function have been made to outline those structural and electronic factors responsible for control of metal-ion reactivity. The interaction of the porphyrin ring of haemoglobin and myoglobin with the nearby amino-acid environment through hydrophobic contacts is examined with regard to the results of magnetic susceptibility, paramagnetic resonance and polarised single-crystal absorption spectroscopic investigations. The interaction of substituted metal ions in carboxypeptidase A with the carbonyl group of substrates in peptide hydrolysis is discussed with reference to their d orbital electron configuration and co-ordination geometry, and the formation of an ordered-solvent structure near the substituted Co(II) ion catalytically active in carbonic anhydrase is suggested to be responsible for the pH-dependent spectral perturbations observed in the electronic absorption spectrum. Correlations of molecular structure, as determined by X-ray diffraction methods, with the electronic structure of the metal–ligand co-ordination centre, as assessed from spectroscopic investigations, thus illustrate the origins of structural control of metal-ion reactivity in proteins and enzymes.

Several problems pertinent to each metal-ion-requiring protein or enzyme have been outlined which, while still relatively poorly understood, are none the less important in understanding the chemical and structural basis of metal function. Some aspects of the theoretical considerations, spectroscopic investigations and high-precision structural data necessary to bring further insight into these problems have been outlined. These problems may be of particular interest to theoretical, co-ordination and structural chemists alike in the investigation of biological roles of metal-ion function.

C. A. McAuliffe (ed.), *Techniques and Topics in Bioinorganic Chemistry*