

CONCLUSIONS

Models for Zn(II)-containing metalloenzymes have been studied in order to obtain information on the mechanism of these metalloenzymes. The acidity of water molecules coordinated to these Zn(II)-metalloenzymes has been the primary focus of this research. It is shown that the acidity of coordinated water molecules has been increased due to the lowering of the C.N. from 6 in the aquo ion to 4 in the complex. This becomes important for metalloenzymes to function at biological pH. Using potentiometry and differential pulse voltammetry, we have studied the increased acidity of models for Zn(II)-metalloenzymes.

Two ligands were studied in order to model these Zn(II)-metalloenzymes. Both PATH and cyclen generate chemical environments similar to the ones found in biological systems. The ligand PATH contains a thiolate group, which has been shown to increase the acidity of the coordinated water molecule, not lower the acidity as previously hypothesized. Of particular importance is the discovery of the pK_a for PATH, which is a N_2S type ligand. To our knowledge, this is the first time that the pK_a for a N_2S -(thiolate)ZnOH has been calculated, leading to the first kinetic and thermodynamic measurements of a series of zinc models for proteins.⁵¹ A Zn-cyclen complex was also found to increase the acidity of coordinated water molecules. The complex was also found to strongly bind a series of ligands which indicates an increase in the acidity of the complexed Zn metal ion. This increase in acidity indicates that the Zn center has become 'softer' in the HSAB classification described by Pearson than is the case of the Zn(II) aquo ion. Therefore, it is concluded that the increased acidity of coordinated water molecules can be attributed to the 'softer' Zn metal ion center found in metalloenzymes.