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THE INFLUENCE OF ELECTROSTATIC INTERACTIONS BETWEEN BURIED GROUPS ON THE STRUCTURE AND PROPERTIES OF GLOBULAR PROTEINS

Electrostatic interactions are generally recognised to be a central feature of the structure and function of many proteins even though they are poorly understood. One class of such interactions, those involving charges buried within a protein, are of especial importance to many metalloproteins, particularly redox proteins. This is because most redox centres are buried within the protein and carry a charge in at least one of its biochemically important oxidation states. The presence of the buried charges may have important consequences for the structure and properties of the protein and this will be demonstrated by reference to the monohaem Class I cytochromes *c*.

The most commonly studied Class I cytochrome *c* mitochondrial cytochrome *c* but there are many bacterial analogs. These are characterised by a common protein fold that results in the burial of most of the haem and its axial ligands. Not only is the iron buried, but at least one of the haem propionates is as well. In some of these cytochromes, the buried propionate is ionised. Experimental observation demonstrate the importance of these buried charges in

1) controlling the level of the redox potential;
2) coupling the change in oxidation state to the protein conformational state;
3) modulating the protein stability.

The general significance of these observations will be considered with reference to other kinds of redox proteins.

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STRUCTURES OF GLYCINATO COMPLEXES OF BIOCHEMICALLY IMPORTANT DIVALENT TRANSITION-METAL IONS IN SOLUTION

Structures of mono-, bis- and tris(glycinato) complexes of biologically important divalent transition-metal ions such as nickel(II) [1,2], copper(II) [3], and zinc(II) [2,4] ions were determined by the X-ray diffraction [1,3,4] and EXAFS [2] methods *in solution* at 25°C. The structural data of these complexes are summarized in Table I. The structure of the bis(glycinato)copper(II) complex was not determinable even by the EXAFS method because of its low solubility in water.

All the complexes investigated were octahedral. The length of an $M^{2+}-OH_2$ bond increased with the introduction of glycinato ions in the coordination sphere of the M^{2+} ion, as we have seen in the case of ethylenediamine complexes of the metal ions [5-8]. Thus, water molecules coordinated to a metal ion became more labile and easier replaceable with an entering ligand at the formation of a higher complex than a lower one.

In the mono(glycinato)copper(II) complex [3], the axial Cu-OH_2(ax) distance was longer than the equatorial Cu-OH_2(eq), Cu-O(eq) and Cu-N(eq) distances (O and N denote carboxylic oxygen and amino nitrogen atoms, respectively, within a chelated glycinato ion). Therefore, the mono-complex had a distorted octahedral structure. On the other hand, the tris-complex, $Cu(gly)_3^-$, was regular octahedral.

All the zinc(II) complexes with glycinato ions were regular octahedral and the Zn-O and Zn-N distances were practically invariable with varying numbers of glycinato ions in the coordination sphere. On the contrary, the nickel(II) glycinato comple-

Table I

M-OH_2, M-O and M-N bond lengths (A) in the $M(gly)_m(H_2O)_n^{(2-m)+}$ complexes in aqueous solution at 25°C

Complex	Ni^{2+}	Cu^{2+}	Zn^{2+}
$M(H_2O)_6^{2+}$	M-O : 2.04	M-O_{eq} : 1.94 M-O_{ax} : 2.43	M-O : 2.08
$M(gly)(H_2O)_n^+$	n = 4 M-OH_2 : 2.08 M-O : 2.09 M-N : 2.09	n = 4 M-$OH_{2,eq}$: 1.98 M-$OH_{2,ax}$: 2.27 M-O : 1.99 M-N : 1.99	n = 4 M-OH_2 : 2.12 M-O : 2.12 M-N : 2.12
$M(gly)_2(H_2O)_n$	Crystal n = 2 M-OH_2 : 2.10 M-O : 2.06 M-N : 2.08 EXAFS n = 2 M-OH_2 M-O : 2.04 a) M-N	—	EXAFS n = 2 M-OH_2 M-O : 2.07 a) M-N
$M(gly)_3^-$	M-O : 2.03 M-N : 2.14 EXAFS M-O : 2.01 M-N : 2.10	M-O : 2.02 M-N : 2.02	EXAFS M-O : 2.12, 2.13 M-N : 2.12, 2.13

a) not separable into each distance.