Structure of Oxy- and Deoxy-Erythrocruorin at 1.4 Å Resolution.

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The crystal structure of erythrocruorin has been refined by constrained refinement at 1.4Å resolution in the following ligand states: aquomet, cyanomet, carbon monoxy, deoxy (1) and oxy (2). Recently restrained refinement (3) with further improvement of the structures has been applied to the deoxy and oxy data. The corresponding R-values are 0.169 and 0.173. The errors of the coordinates are less than 0.1Å in the interior of the molecule. The r.m.s. differences between the deoxygenated and oxygenated erythrocruorin are about 0.1Å. The changes in the tertiary structure propagate from the location of primary events and often fade out at the molecular surface. Helix E passing the distal side of the heme group is affected most by the direct contact with the ligand bound to the heme iron. The dioxygen is bound to the iron end-on at a distance of 1.8Å. In addition, a water molecule is attached to the dioxygen molecule 2.1Å apart from the terminal oxygen with a bond angle of 135°. This situation may lead to the bond angle iron-dioxygen of 150° being larger than in model compounds. The additional water might be involved in the auto-oxidation process. Due to the bulk of the effective 3-atom ligand not only the distal residues move, but also the whole heme group is pushed slightly (0.05Å) to the proximal side. This, in turn, causes a movement of the proximal histidine and its adjacent residues with a main component away from the heme. The opposite movements of the distal and the proximal side lead to a slight (<0.2Å) opening of the heme pocket at the ligand binding position. The protoporphyrin is both in the deoxy and in the oxy form significantly non-planar. The type of distortion may best be described by quasi-S_4 ruffling and, additionally, slight doming. The electron density map indicates a higher degree of puckering for the oxy form, although this has not yet been quantified. The distances of the iron from the heme plane are 0.2Å in deoxy and 0.3Å in oxy, which is opposite to the movements on other ligation (1). The unusual displacement of the iron from the heme plane together with the ruffling of the porphyrin are an experimental indication that conformational changes in the heme may play an important role in the trigger mechanism (4). Spin state changes of the iron seem to be tolerated by the porphyrin without pronounced iron movements. The dominant role for the tertiary structural changes upon ligation may be ascribed to the steric interactions between the ligand and the globin.

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