A New Covalent Albumin-Hemin Complex Mimics Peroxidase Activity

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The ability of albumin to bind hemin has stimulated efforts to develop albumin-hemin complexes that mimic the reversible oxygen-binding properties of heme proteins such as in electron transfer reactions, oxygen transport and storage, and a variety of oxidation processes that use dioxygen, hydrogen peroxide, or alkyl peroxides as terminal oxidants. Here, we have produced a new covalent Albumin-Hemin complex. Hemin, having two carboxyl groups, was chemically coupled with bovine serum albumin (BSA) through the ester bond formed with carbodiimide. The spectroscopic and reactivity properties of the covalent BSA-hemin complex have been investigated. Free hemin electronic absorption spectrum exhibits the typical features of Fe(III) high-spin species with water molecules as axial ligands: Soret band at 388 nm, Qβ-band at 498 nm, Qα-band almost absent, and charge transfer band at 610 nm. In comparison, the spectrum of hemin appended to BSA recorded in the same conditions, exhibited a broadened Soret band shifted to 402 nm, and detectable Qα-band at 530 nm. The insertion of hemin occurred without any significant change in the far-UV CD features of the BSA, but its insertion added CD pattern in the Soret region (360-460 nm). The electronic spectral properties and especially the added CD pattern in the Soret region reflects the location of hemin in a hydrophobic microenvironment provided by folded albumin protein chain. As expected, BSA-hemin complex was activated to high valence species by hydrogen peroxide, a typical peroxidase reaction. The complex BSA-hemin has potential application as a peroxidase catalyst and may have biological relevance. (Supported by CAPES, CNPq and FAPESP).