

Metallobiliverdin radicals-DFT studies.

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Streszczenie

Several aspects of the molecular and electronic structure of biliverdin derivatives have been studied using density functional theory (DFT). The calculations have been performed for complexes of trianion $(\text{BvO}_2)^{3-}$ and dianion $[\text{BvO}(\text{OH})]^{2-}$, derived from two tautomeric forms of biliverdin, BvO_2H_3 and $[\text{BvO}(\text{OH})]\text{H}_2$, with redox innocent metal ions: lithium(I), zinc(II), and gallium(III). One-electron-oxidized and -reduced forms of each complex (cation and anion radicals) have been also considered. The molecular structures of all species investigated are characterized by a helical arrangement of tetrapyrrolic ligands with the metal ion lying in the plane formed by the two central pyrrole rings. The spin density distribution in four types of metallobiliverdin radicals— $[(\text{BvO}_2\cdot)\text{M}^{n+}]^{n-2}$, $[\{\text{BvO}(\text{OH})\}\text{M}^{n+}]^{n-1}$ (cation radicals), $[(\text{BvO}_2\cdot)\text{M}^{n+}]^{n-4}$, $[\{\text{BvO}(\text{OH})\}\text{M}^{n+}]^{n-3}$ (anion radicals)—has been investigated. In general, the absolute values of spin density on *meso* carbon atoms were larger than for the β -carbon atoms. Sign alteration of spin density has been found for *meso* positions, and also for the β -carbon atoms of at least two pyrrole rings. The calculated spin density maps accounted for the essential NMR spectroscopic features of iron biliverdin derivatives, including the considerable isotropic shifts detected for the *meso* resonances and shift alteration at the *meso* and β -positions

Adres publiczny

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