

Some peculiarities of the paramagnetic dinitrosyl non-heme iron complexes structure

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Endogenous compounds including into nitrogen oxide (NO) and weakly-bounded form of iron are capable participate in the various physiological processes into organism such as vazodilatation, aggregation of trombocytes, regulation of arterial pressure. They are formed paramagnetic centres which characterized by an ESR signal with $g_{av} \sim 2.03$ and may be identified as 2.03 complexes according to the average value of the g-factor. These complexes including into two nitrogen oxide molecules and two paired RS groups of proteins are represented low spin mononuclear complexes ($S=1/2$) and can be consider as only from of coexistence of most important intracellular components – loosely bound form of nonhaem iron and nitrogen oxide. On the base of the complex using of methods quantum chemistry, theoretical conformational analysis and ESR, the spatial structure of iron protoxide dinitrosyl complex with cysteine (IPDCC) has been investigated.

For calculation we used the IPDCC model suggested by the results of ESR spectra analysis in which a ferrous atom is coordinated by two nitrosyl groups and two sulphur atoms of the cysteine's thiol groups.

According to the calculation results dinitrosyl non-heme iron complex is characterized by deformation of the plane-square orientation of ligands in the complex due to the drop of one of the sulphur atoms out of the assumed quadratic. The obtained structure is characterized by a nonequivalent distribution of electron density between nitrosyl and thiol groups of ligands. The calculation of dissociation energy of nitrosyl groups has demonstrated that they are different in absolute value, thus proving, as in the case of the tetrahedral structure, the preference of dissociation of NO-groups with a localized total negative charge. Thus the obtained results prevent the unambiguous choice between IPDCC structures with distorted tetrahedral and distorted quadratic coordination of the central atom relative to two nitrosyl groups and two sulphur atoms of thiol groups in cysteine proving the nonequivalency of these ligands in complex and explaining the contradiction which appears while interpreting the obtained experimental results based on different approximations. One of the factor which do not appear in the ESR spectrum but influence on the 2.03 complexes symmetry is the inclusion of one or two water molecules into 2.03 complexes. It was obviously from the results of calculation that the consecutive addition of first and then the second water molecules are the factor which stabilize the structure of dinitrosyl iron complexes without any effect on its geometry. According to the results of calculation of dinitrosyl iron complexes are six-coordinated complexes distorted octahedral structure of which characterized by the non equivalency of electron density distribution of $Fe^{2+} - NO$ bonds. The obtained results based on the ESR, theoretical conformational analysis and quantum chemistry methods make it possible assert that the study of the mechanism and conditions of forming six-coordinated dinitrosyl iron complexes can be considered as the model of process of influence of intracellular environment on 2.03 complexes structures formed in animal tissues.