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## Modeling of Complex Formation Equilibria and Proton and Ligand Exchange Reactions in Aqueous Solutions of Oxovanadium(IV) with L- and DL-Histidine

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### Abstract

For the further development of the magnetic relaxation method, the STABLAB program was implemented, which makes it possible to calculate both thermodynamic equilibrium parameters and kinetic characteristics of the proton and ligand exchange reactions from the results of parallel measurements of the spin relaxation times  $T_1$  and  $T_2$ , of solvent nuclei. With this program, the nuclear magnetic relaxation data on water protons were used to calculate the stability constants and proton and ligand exchange rates for the complexes formed in the oxovanadium(IV)-L-histidine (LH) and oxovanadium(IV)-DL-histidine systems at pH 0.5-10: VOLH, VO(LH)<sub>2</sub>, VOL, VOL<sub>2</sub>H, VOL<sub>2</sub>, VOL<sub>2</sub>H<sub>1</sub>, and (VO)<sub>2</sub>L<sub>2</sub>H<sub>2</sub>. The structures of these complexes were determined based on the comparison of isotropic EPR parameters, stability constants, and molar proton relaxation coefficients. LH is coordinated in the equatorial plane of oxovanadium(IV) through the NH<sub>2</sub> and COO<sup>-</sup> groups or through the imidazole nitrogen atom and the carboxy group; both of these coordination modes concurrently occur in the VO(LH)<sub>2</sub> structure. The occurrence of two ligands exerts a synergistic effect on stabilization of the VO(LH)<sub>2</sub>, VOL<sub>2</sub>H, and VOL<sub>2</sub> bis-complexes, which is explained by the effect of d- $\pi$  bonding in the complexes with the trans arrangement of the imidazole nitrogen atom of one ligand and the COO<sup>-</sup> group of the other ligand in the equatorial plane. This d- $\pi$  bonding is the main cause of some other unusual effects - the stereoselectivity in the formation of the VOL<sub>2</sub> complex and the fast spontaneous proton exchange for VOL<sub>2</sub>H-1. In the proton exchange reactions, the enhanced kinetic activity of the LH<sub>2</sub> form is attributed to the occurrence of the intraligand microequilibrium of the proton migration from the imidazole moiety to the carboxy group in interaction with VO<sub>2</sub><sup>+</sup> and to the fast interligand proton transfer in interaction with VOLH. A significant stereoeffect in the ligand exchange reactions was found for the first time: the rate constant of the exchange between VOL<sub>2</sub> and L in solutions with L-histidine is 1.5 times the constant in solutions with DL-histidine. This is rationalized by the fact that the imidazole nitrogen atom in the VOL<sub>2</sub> meso form efficiently protect the axial position from the attack of the entering ligand. The extremely high kinetic activity of the LH form in the ligand exchange with the oxovanadium(IV) complexes as compared to the complexes of other metal ions is attributed to a special mechanism that implies the formation of the hydrogen bond involving the protonated nitrogen atom of LH and the oxygen atom of V=O, as well as to a rather high nucleophilicity of the imidazole nitrogen atom of LH.

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