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The structures of dimeric stereoisomeric tartrates of iron(III) as determined by molecular mechanics calculations

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Abstract

The stereospecific formation of iron(III) complexes with *d*- and *dl*-tartaric acids (dH_4L, dlH_4L respectively) is discussed. Molecular mechanics calculations (MIND program, model of Dashevsky–Plyamovatyi) are applied to modelling of dimeric tartrate $Fe_2(d\text{-}L)_2^{2-}$ and $Fe_2(d\text{-}L)(l\text{-}L)^{2-}$(II) structures. Stereospecific formation is explained by lesser values of energy of rigid iron(III) octahedral coordination in (I).

1. Introduction

The formation of iron(III) tartrates has been reported in a considerable number of works [1–4]. At pH 2–5, complex forms of iron(III) tartrates undergo interconversion in the conventional manner. A dimeric form $Fe_2L_2^{2-}$ (where L^{4-} is the rest of the tartaric acid H_4L, $C_4H_6O_6$) occurs in aqueous solutions in this pH region. The same scheme was used by us in our investigations of stereoselective and stereospecific effects of formation of iron(III) with stereoisomeric *d*- and *dl*-tartaric acids.

The *dl*-dimeric tartrate $Fe_2(d\text{-}L)(l\text{-}L)^{2-}$ was demonstrated by methods of proton magnetic relaxation and pH measurements with mathematic simulations as in Ref. [3]. From stability data it is shown that *d*-dimeric tartrate is not formed, in spite of the *dl*-dymeric tartrate. To explain this fact we used molecular mechanics calculations in the program MIND whose results models are described in Ref. [5].

2. Experiments and results

The molecular mechanics study was accomplished using the program MIND. In the present work we used the molecular mechanics method which takes into consideration interactions between heteroatom electron lone pairs [6]. This method, called the Dashevsky–Plyamovatyi model [5,7], and in the force field of that model, the steric energy E of the system is presented in the expression in Eq. (1).

$$E = \frac{1}{2}\sum_i K_{l_i}(l_i - l_0)^2 + \frac{1}{2}\sum_i K_{\alpha_i}(\alpha_i - \alpha_0)^2 + \frac{1}{2}\sum_i V_i[1 + x\cos(n_i\varphi_i)] + \sum_{i>j}\sum[-ar_{ij}^{-b} + b\exp(-cr_{ij})] \quad (1)$$

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