

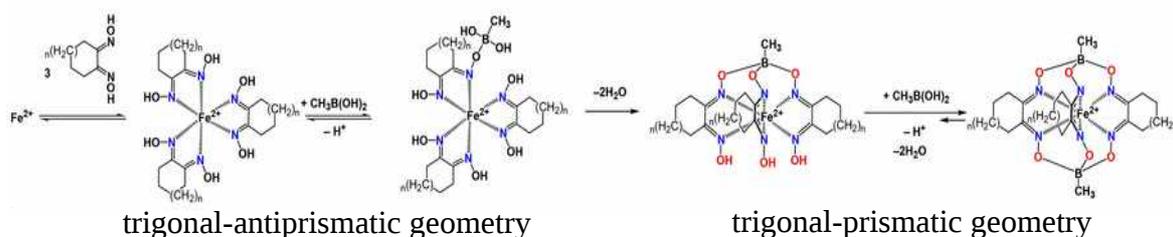
Kinetics of the template synthesis and acidic decomposition of the methylboron-capped iron(II) tris-dioximate clathrochelates: dramatic changes in the kinetic parameters and schemes in passing from six- to eight-membered alicyclic α -dioximes

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Reaction of the template synthesis of the boron-capped iron(II) macrobicyclic complexes (clathrochelates) of a general formula $\text{FeD}_3(\text{BR})_2$ (where D^{2-} is the alicyclic α -dioximate dianion, R is the apical substituent) are known [1–3] to be the unique objects for studying of the kinetics of their coordination-driven self-assembly from three chelating and two cross-linking ligand synthones on the iron(II) ion as a matrix (Scheme). These reactions proceed in the quantitative yields even in diluted solutions, thus giving the intensively colored ($\epsilon \sim 2 \cdot 10^4 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) clathrochelate products with their absorption maxima from 440 to 460 nm, whereas the initial ligand synthones are optically silent in a given range. This allows an easy studying of both their synthesis and decomposition using a photometric method. We performed these reactions for the methylboron-capped iron(II) clathrochelates – the derivatives of alicyclic six-, seven- and eight-membered α -dioximes. Their ring size was found to dramatically affect the kinetic schemes and parameters of the template synthesis and acidic decomposition reactions of these clathrochelates. If the general schemes of their coordination-driven self-assembly persist, those for six- and seven-membered α -dioximes contain a rate-determining stage, whereas that for their eight-membered analogue has three initial consecutive stages with close reaction rates. Passing from a six-membered chelating synthon to its seven-membered analogue causes a decrease in the synthesis reaction rates by approximately three orders of magnitude. These kinetic effects were explained using the single-crystal XRD data for the initial α -dioximes and for their methylboron-capped macrobicyclic iron(II)-encapsulating derivatives as well.



[1] Y.Z. Voloshin, N.A. Kostromina, R. Krämer, *Clathrochelates: Synthesis*,

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[3] A.L. Pomadchik, A.S. Belov, E.G. Lebed, I.G. Belaya, A.V. Vologzhanina, Y.Z. Voloshin, *Molecules* **2021**, *26(13)*, p. 4019.

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