




# Mössbauer study of some novel iron-bis-glyoxime and iron-tris-glyoxime complexes

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## Abstract

Dioximes as ligands are used as analytical reagents and serve as models for biological systems as well as catalysts in chemical processes. A number of novel mixed complexes of the type  $[\text{Fe}(\text{DioxH})_2(\text{amine})_2]$  have been prepared and characterised by FTIR,  $^{57}\text{Fe}$  Mössbauer and mass spectroscopy by us. We have found strong Fe–N donor acceptor interactions and iron occurred in low-spin  $\text{Fe}^{\text{II}}$  state in all complexes. Later, we have also found that the incorporation of branching alkyl chains (isopropyl) in the complexes alters the Fe–N bond length and results in high-spin iron(II) state [1, 2]. The question arises: can the spin state of iron be manipulated generally by replacing the short alkyl chains with high volume demand ones in Fe-azomethine-amine complexes? To answer the question we have synthesized novel iron-bis-glyoxime and iron-tris-glyoxime complexes when long chain alkyl or aromatic ligands replaced the short alkyl ones and studied by  $^{57}\text{Fe}$  Mössbauer spectroscopy, MS, FTIR, UV-VIS, TG-DTA-DTG and XRD methods. Novel iron-bis-glyoxime and iron-tris-glyoxime type complexes,  $[\text{Fe}(\text{Diethyl-Diox})_3(\text{BOH})_2]$ ,  $[\text{Fe}(\text{Diethyl-Diox})_3(\text{BOEt})_2]$  and  $[\text{Fe}(\text{phenyl-Me-Diox})_3(\text{BOEt})_2]$ , were synthesized similarly as described in [2]. The FTIR, UV-VIS, TG-DTA-DTG and MS measurements indicated that the expected novel complexes could be successfully synthesized.

**Keywords** iron<sup>II</sup>-dioximes ·  $^{57}\text{Fe}$  Mössbauer spectroscopy · Low spin- · High spin  $\text{Fe}^{\text{II}}$  states

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## 1 Introduction

The unique properties of a metal ion encapsulated in the cage of a macropolycyclic ligand and isolated from the influence of external factors have allowed the use of clathrochelates as models of important biological systems, electron carriers, and catalysts of photochemical and redox processes [3].

Several iron chelates have been reported for application in the treatment of thalassaemia, other transfusion-dependent diseases, and also used as MRI contrast agents. Other iron complexes are also known for their antibacterial, antifungal and biomimetic activities [4].

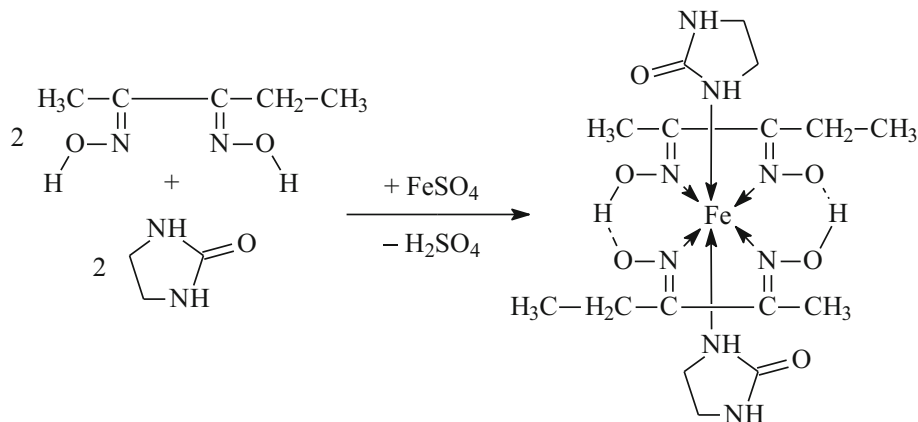
The  $[M(\text{Diox})_3(\text{BOR})_2]$  type complexes were discovered by Schrauzer. Voloshin et al. prepared a series of  $[\text{Fe}(\text{Glyox})_3(\text{BOR})_2]$  type complexes under soft conditions with a high yield, and characterized with physical-chemical methods, like XRD, IR-, NMR-, Mössbauer- and electron spectroscopy. Transition metal containing clathrochelates are used in HIV infection treatment [5].

## 2 Experimental

Novel two type complexes:  $[\text{Fe}(\text{DioxH})_2(2\text{-imidazolidone})_2]$  and  $[\text{Fe}(\text{Diox})_3(\text{BOR})_2]$  were synthesized by reacting iron(II)-salt with  $\alpha$ -dioxime, amine or boric acid in the corresponding solvent. The details of synthesis:

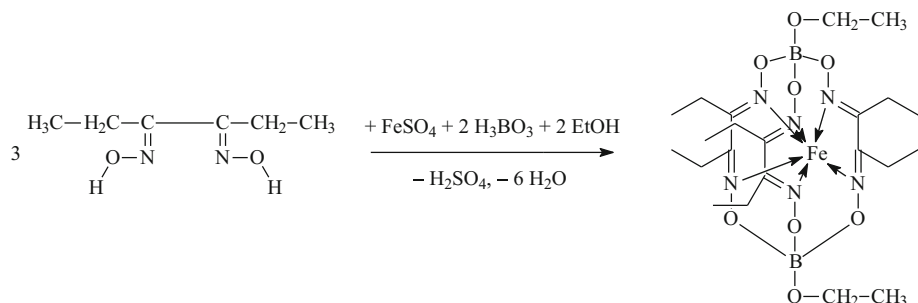
- *Synthesis of  $[\text{Fe}(\text{DioxH})_2(\text{amine})_2]$  type complexes*

0.005 mol Et-Me-DioxH<sub>2</sub> or Me-i-Pr-DioxH<sub>2</sub> was dissolved in 20 ml EtOH and this solution was added to the aqueous solution of 0.001 mol (0.3 g)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 0.4 g ascorbic acid dissolved in 10 ml water. The role of ascorbic acid is to prevent the oxidation of  $\text{Fe}^{\text{II}}$  to  $\text{Fe}^{\text{III}}$ . After that 0.002 mol amine (2-imidazolidone) dissolved in 5 ml EtOH was added. The obtained solution was heated for 2–3 h on a water bath under inert atmosphere. The filtered crystalline complexes were washed with EtOH–water mixture (1:1) and diethyl ether. A typical reaction as an example:



• *Synthesis of  $[Fe(Diox)_3(BO-R)_2]$  type complexes*

0.0075 mol diethyl-dioxime or Me-Ph-DioxH<sub>2</sub> was dissolved in 20 ml EtOH, then this solution was added to an aqueous solution of 0.0025 mol (0.7 g) FeSO<sub>4</sub> and 0.4 g ascorbic acid dissolved in 25 ml water. Afterwards 0.0075 mol (0.46 g) boric acid dissolved in 15 ml H<sub>2</sub>O was added. The mixture was refluxed for 15 min under inert atmosphere, and then 0.00375 mol (1.4 g) borax dissolved in 15 ml distilled water and 55 ml ethyl-alcohol or water were added. The obtained solution was heated for 2–3 h on a water bath, under inert atmosphere. After cooling the crystalline complexes were filtered off, washed with the used ethyl-alcohol or distilled water and diethyl ether, then dried in air. A typical reaction is shown below:



The <sup>57</sup>Fe Mössbauer measurements of these complexes were carried out with a conventional constant acceleration (WISSEL) Mössbauer spectrometer using integrated multichannel analyzer and scintillation detection in transmission geometry. The samples were measured at 78 K and 293 K temperatures by means of a JANIS liquid helium cryostat. A <sup>57</sup>Co source of 0.8 GBq activity in Rh matrix supplied the gamma rays. The isomer shift values are given relatively to  $\alpha$ -iron at room temperature. The analysis of the Mössbauer spectra was carried out with the MOSSWINN 4.0 code [6].

The IR spectra were recorded with a Bruker Alpha (Platinum single reflection diamond ATR) and Perkin–Elmer System 2000 FTIR spectrometer at room temperature, in the wave-number range of 4000–400 cm<sup>-1</sup>. The samples were measured in solid state (in powder form) or in KBr pellets, respectively.

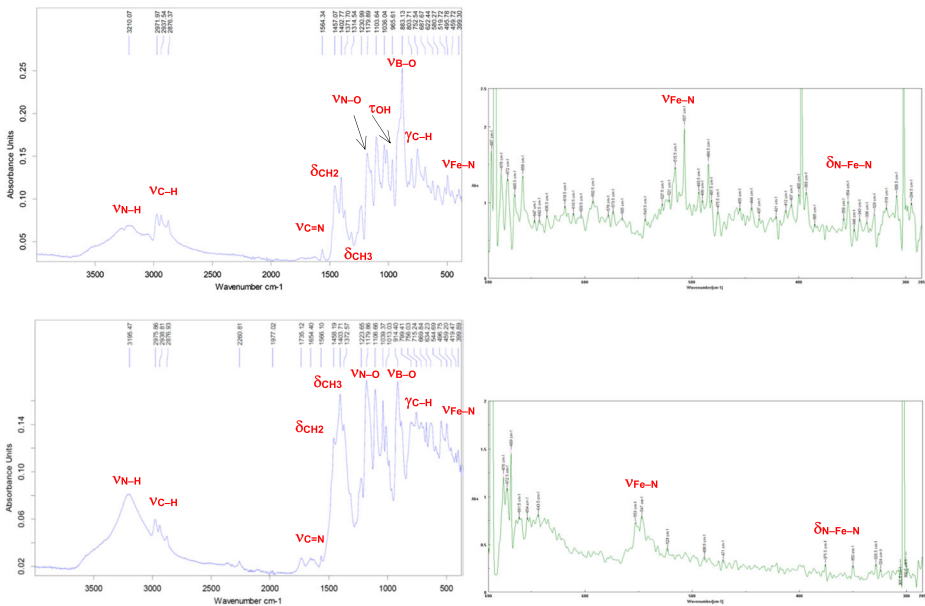
Thermal measurements were performed with a 951 TG and 910 DSC calorimeter (TA Instruments), in air atmosphere, at a heating rate of 10 K·min<sup>-1</sup> (sample mass 4–10 mg).

Mass spectrometric (MS) measurements were carried out by a PE Sciex API 2000 triple quadrupole mass spectrometer, using electrospray ionization (ESI) in the 200–1200 m/z region.

The powder XRD measurements were performed with a PANalytical X'pert Pro MPD X-ray diffractometer.

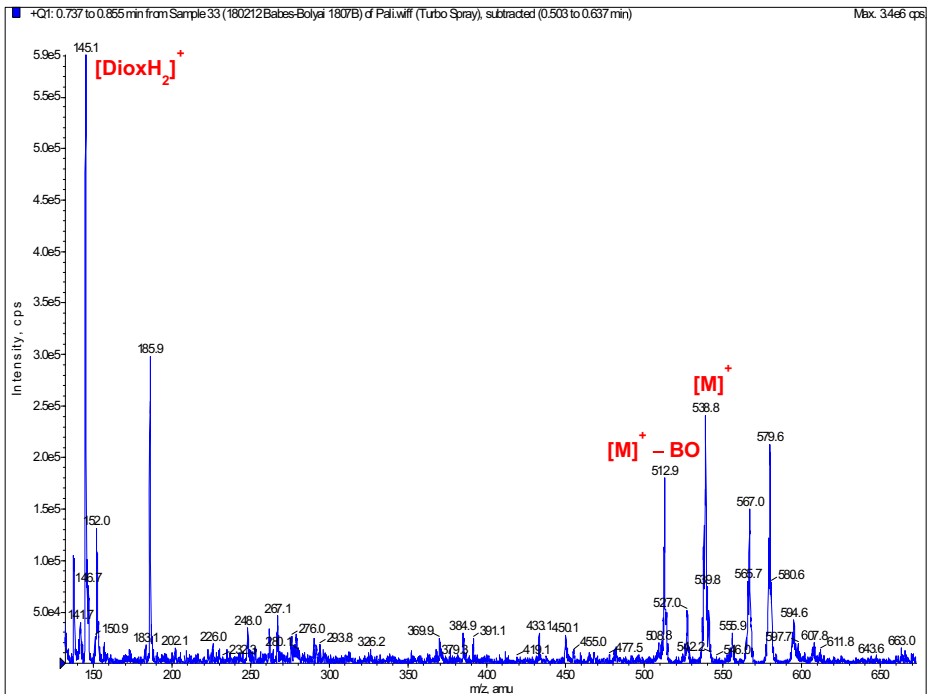
### 3 Results and discussion

Novel iron(II)-tris-glyoxime complexes according their above given structure were successfully synthesized. This is demonstrated by IR (Fig. 1), MS (Fig. 2) and TG (Fig. 3) spectra of selected samples.



**Fig. 1** IR-spectra of  $[\text{Fe}(\text{Diethyl-Diox})_3(\text{BOH})_2]$  (top),  $[\text{Fe}(\text{Diethyl-Diox})_3(\text{BOEt})_2]$  (bottom)

The IR spectra (Fig. 1) reveal the presence of Fe-N and C=N bonds based on their characteristic vibrational bands of the complexes.



**Fig. 2** MS-spectrum of  $[\text{Fe}(\text{Diethyl-Diox})_3(\text{BOH})_2]$

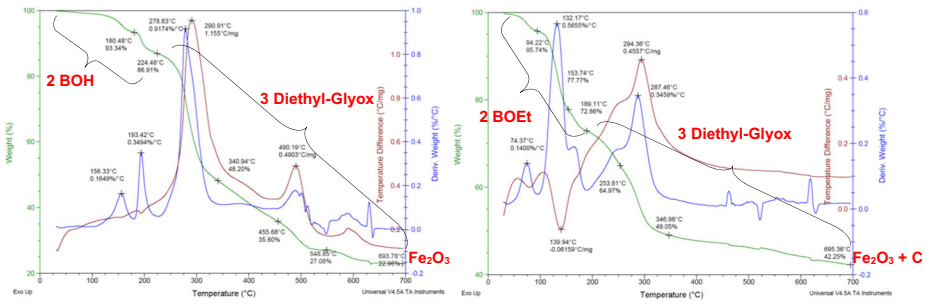


Fig. 3 TG-DTG-TGA measurements  $[Fe(Diethyl-Diox)_3(BOH)_2]$  (left) and  $[Fe(Diethyl-Diox)_3(BOEt)_2]$  (right)

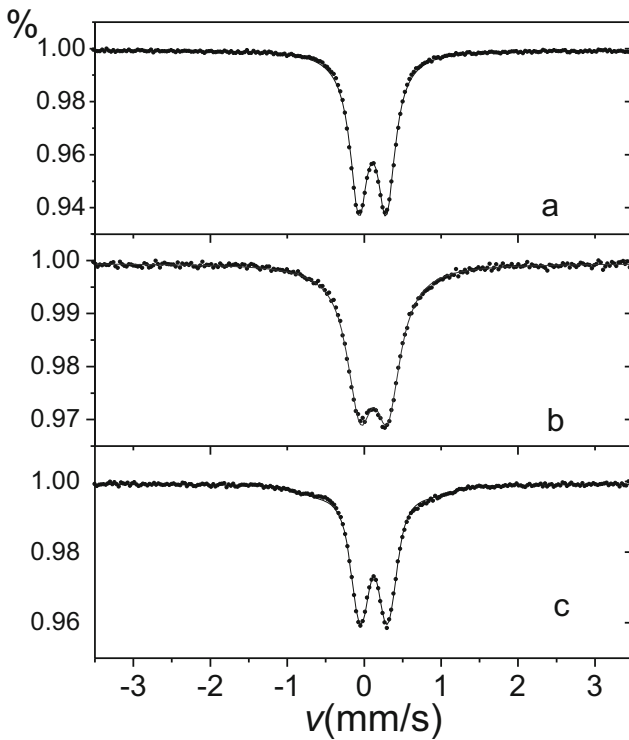
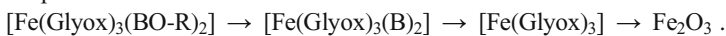


Fig. 4 80 K  $^{57}Fe$  Mössbauer spectra of  $[Fe(Diethyl-Diox)_3(BOH)_2]$  (a),  $[Fe(Diethyl-Diox)_3(BOEt)_2]$  (b) and  $[Fe(phenyl-Me-Diox)_3(BOEt)_2]$  (c)

The very intense peaks of molecule ion and ligand fragments in the MS spectrum (Fig. 2) well indicate that the expected compound was prepared.

The thermoanalytical measurements (Fig. 3) show the mechanism of thermal decomposition.



$^{57}Fe$  Mössbauer spectra of iron(II)-tris-glyoxime complexes are shown in Fig. 4. The spectra could be evaluated by a one doublet model indicating that there is only single Fe-environment in the samples. The Mössbauer parameters of the compounds are shown in

**Table 1** Mössbauer parameters of iron-tris-gloxime and iron-bis-gloximes

Compound	Meas. Temperature T (K)	Isomer shift, $\delta$ (mm/s)	Quadrupole splitting $\Delta$ (mm/s)	Line width, $W$ (mm/s)	Spin state	Refs.
[Fe(Diethyl-Diox) <sub>3</sub> (BOH) <sub>2</sub> ]	295	0.07±0.003	0.33±0.01	0.29±0.01	LS	
	80	0.10±0.003	0.35±0.01	0.28±0.01		
[Fe(Diethyl-Diox) <sub>3</sub> (BOEt) <sub>2</sub> ]	295	0.08±0.003	0.34±0.01	0.34±0.01	LS	
	80	0.12±0.003	0.35±0.01	0.40±0.01		
[Fe(phenyl-Me-Diox) <sub>3</sub> (BOEt) <sub>2</sub> ]	295	0.09±0.003	0.44±0.01	0.35±0.01	LS	
	80	0.13±0.003	0.48±0.01	0.38±0.01		
[Fe(Me-i-prop-gloxH) <sub>2</sub> (2-imidazolidone) <sub>2</sub> ]	80	1.24±0.002	2.68±0.01	0.29±0.01	HS	[1, 2]

Table 1. These Mössbauer parameters revealed that iron is solely in low spin iron(II) state in all the three complexes.

The results can be discussed by asking the question why the incorporation of relative high volume demand alkyl chains or aromatic rings in the iron-tris-glyoximes do not alter the Fe–N interatomic distances to be critical for appearance of high spin iron(II) state, dissimilarly as found earlier [1, 2] in the case of iron-bis-glyoximes.

In the case of iron-bis glyoximes [1, 2] it was shown that high spin Fe<sup>II</sup> state occurred (Table 1) when branched chain ligand was built in the dioxime plane. The reason that the high-spin state in the planar iron-bis-glyoxime complex containing the higher-volume demand branched-chain ligand become more favorable is that the larger-volume demand ligands change the molecular geometry in such a way that the bond distances between the planar nitrogen atoms and the iron atom increase. The Mössbauer parameters of [Fe(Me-i-Pr-DioxH)<sub>2</sub>(2-imidazolidone)<sub>2</sub>] clearly indicate high spin state in Table 1.

The distribution of electrons on 3d shell in low-spin and high-spin configurations in Fe<sup>II</sup> and their enthalpy curves are the function of iron-ligand distance. Mössbauer spectroscopy can be used as a diagnostic method to determine spin state in Fe<sup>II</sup> iron complexes.

For the studied Fe(Diox)<sub>3</sub>(BOR)<sub>2</sub>] type complexes one can assume that the O<sub>3</sub>BOR moiety creates a rather rigid structure for the complex molecule setting a short Fe–N distance, and this is responsible for the high ligand field splitting and low spin ground state for iron. The rigid structure does not allow substantial influence of the alkyl groups (or H), neither on the carbon atoms of the glyoxime nor on the BO group, on the Fe–N distance and therefore on the spin state. The LS state is preserved.

In the case of bis-glyoxime complexes, as we found earlier [1, 2] a high volume demand branching alkyl chain, like isopropyl on the carbon atom of the glyoxime resulted in high spin state. It is logical to assume that the planar bis-glyoxime moiety is flexible enough to get distorted by large alkyl groups, and in a non-planar structure the electron donation from the ligand to the 3d shell of iron is less effective, the formal ligand strength decreases, and the preferred spin state will be high spin.

## 4 Conclusion

Novel iron(II)-tris-glyoxime complexes involving high volume demand ligands were successfully synthesized.

$^{57}\text{Fe}$  Mössbauer spectroscopy indicated the occurrence of iron in solely low spin iron(II) state in all compounds. This can be explained by the less flexible spatial molecular structure of iron(II)-tris-glyoxime complexes compared to that of planar iron(II)-bis-glyoxime compounds. The alteration of the Fe–N bond length upon incorporation of even a rather high volume demand ligand is smaller than needed for a spin transition from LS to HS.

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## Declarations

**Conflict of interest** Authors declare that no conflict of interest exists related to their paper entitled Mössbauer study of some novel iron-bis-glyoxime and iron-tris-glyoxime complexes to be published in the *Hyperfine Interactions*. Authors declare that our paper entitled Mössbauer study of some novel iron-bis-glyoxime and iron-tris-glyoxime complexes contains novel scientific statements which have not been published yet.

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