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Moessbauer study of tris-(methyldiethoxysiloxy)iron and its derivatives

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Abstract. Moessbauer study of tris-(methyldiethoxysiloxy)iron, \([\text{CH}_3(\text{C}_2\text{H}_5\text{O})_2\text{SiO}]_3\text{Fe}\), tris(polymethylsiloxy)iron, \([\{\text{CH}_3[(\text{CH}_3)\text{SiO}]_4]\_2\text{CH}_3\text{SiO}_3\}_3\text{Fe}\), and its derivatives with 1-decanthiol showed, that these compounds are the complexes of high-spin trivalent iron. The analysis of the spectra by means of Afanas’ev-Chuev method allowed us to suggest different ways for their interpretation.

1. Introduction
Immobilized molecular systems containing iron-centres are very promising for present-day catalysis. The long history of the metallosiloxanes demonstrates evident progress in the molecular design of these prospective compounds [1-3]. But the use of the cage-like metallosiloxanes has limitations due to their insolubility in organics and also due to the crowded coordination sphere of metals’ ions. The new approach based on the sodium salts of organoalkoxysilanes allows us to obtain the spider-like oligomers with a single iron atom as a branching centre. Good solubility in organic solvents combined with the absence of strong ligands in oligomers’ composition makes them prospective intermediates in catalytic applications.

All these substances are maroon liquids being in a viscous-flow state at room temperature. They transform into glass state at lower temperatures with no crystallization taking place. The synthesized samples can contain the impurities of the reactants and/or by-products. They can be sensitive to moisture if containing functional groups. These substances can also exist as a mixture of stereoisomers and intent to oligomerization during the chemical transformations of their functional groups. That is why the number of the techniques which are suitable for the investigation of these compounds is very limited.

The state and the behavior of iron centers within oligomeric structure during their chemical transformations are very important for further applications. Moessbauer spectroscopy is a suitable technique for their investigation. It can allow us to determine the oxidation state of iron, magnetic properties, coordination number, to estimate the purity of the product etc. But for the oligomer samples which have no definite structure and in which the environment of iron atom could be considerably disordered it is not easy to propose correct models for the spectra observed. The model should provide a description of the distributions of quadrupole splittings and isomer shifts, as the existence of these distributions is an inherent property of the compounds with disordered structure. Moreover, during the freezing of the liquid sample, which is necessary to record the Moessbauer
spectrum, the distortion of iron coordination polyhedron can also take place and should be taken into account. Finally, it is necessary to keep in mind the influence of the impurities, because they commonly have similar chemical nature and their lines could be in the same spectral range.

In this report the results of a Moessbauer study of some iron organosiloxanes are presented.

2. Experimental
To synthesize tris-(methyldioethoxysiloxy)iron \([\text{CH}_3(\text{C}_2\text{H}_5\text{O})_2\text{SiO}]_3\text{Fe}\) we used the interaction of \(\text{FeCl}_3\) with sodium oxy(methyl)dietoxysilan \((\text{CH}_3)(\text{C}_2\text{H}_5\text{O})_2\text{SiONa}\):

\[
(\text{CH}_3)(\text{C}_2\text{H}_5\text{O})_2\text{SiONa} + \text{FeCl}_3 \rightarrow [(\text{CH}_3)(\text{C}_2\text{H}_5\text{O})_2\text{SiO}]_3\text{Fe} + \text{NaCl}
\]

This organosiloxan was further treated with nonamethyltetrasiloxan-1-ol \(\text{CH}_3[(\text{CH}_3)_2\text{SiO}]_4\text{H}\) to produce tris(polymethylsiloxy)iron \([\{\text{CH}_3[(\text{CH}_3)_2\text{SiO}]_4\}_2\text{CH}_3\text{SiO}]_3\text{Fe}\):

![Diagram of iron organosiloxane structure]

Finally, this oligomer was treated with different quantities of 1-decanthiol \(\text{CH}_3(\text{CH}_2)_9\text{SH}\) to introduce sulfur to the first coordination sphere of iron. These products as well as two intermediate oligomers were studied by Moessbauer spectroscopy.

The \(^{57}\text{Fe}\) Moessbauer absorption spectra were measured at 77K on a Perseus spectrometer working at constant velocities. A standard \(\gamma\)-source of \(^{57}\text{Co}\) in metallic rhodium matrix with the activity of 0.8 GBk (a product of Cyclotron, Co., Ltd., Obninsk, Russia) was employed. Isomer shifts in this paper are presented relative to \(\alpha\)-Fe.

To fit the Moessbauer spectra we used the DISCVER program based on the Afanas'ev-Chuev method \([4]\) which uses the Voigt profile to fit the line shape. At the first step this program calculates the maximal possible number of well-defined lines in a spectrum with the intended statistical level. It also takes into account the source line-shape and the thickness of an absorber. Then an operator can apply the binding (e.g. doublets etc.) according to the chemical nature of the sample under study.

3. Results and discussion
The Moessbauer spectra obtained for all samples (Figure 1) are slightly asymmetric doublets which can be reliably related to high-spin trivalent iron (Table 1).

The DISCVER program allowed us to fit each of these spectra with one doublet (parameters presented in Table 1). The shapes of the doublet’s lines are described by the Voigt profile

\[
v(v,\Gamma,\gamma) = \frac{1}{2\pi} \frac{1}{\sqrt{\gamma}} \frac{1}{\sqrt{2\pi}} \int \frac{1}{(v-x)^2 + (\Gamma/2)^2} \exp(-x^2/2\gamma^2) \, dx
\]

where \(\Gamma\) is a sum of double natural linewidth and the additional Lorentzian line broadening in the Moessbauer source \((\Gamma = 2\Gamma_0 + \Gamma_\alpha)\), \(\gamma\) is the Gaussian width of the line. According to the suggested model each iron ion in the substance is characterized by the symmetric doublet of two Lorentzians. For all iron atoms in the substance the isomer shifts and quadrupole splittings of the doublet are distributed according to the Gaussian probability function. The scatter of both isomer shift and quadrupole splitting for the substance causes the asymmetry of the doublet, so that two parameters \(\gamma_1\) and \(\gamma_2\) characterize the degree of the disorder. Assuming the linear correlation between scattered values of the isomer shift and quadrupole splitting \(\gamma_0 = \alpha\gamma_\Delta\), one can evaluate the widths of their Gaussian distributions \(\gamma_\delta\) and \(\gamma_\Delta\).
Table 1. Moessbauer parameter of four iron organosiloxanes at 77 K.

| Sample                                                                 | Fit with one doublet | Fit with two doublets |
|------------------------------------------------------------------------|----------------------|-----------------------|
|                                                                       | δ, mm s⁻¹  | Δ, mm s⁻¹  | γΔ, mm s⁻¹  | α  | χ² | δ, mm s⁻¹  | Δ, mm s⁻¹  | S, % | γΔ, mm s⁻¹  | α  | χ² |
| [CH₃(C₂H₅O)₂SiO]₃Fe                                                   | 0.453(4) | 0.881(8) | 0.36 | 0.01 | 1.17 | 0.427(9) | 0.98(2) | 75(5) | 0.44 | 0.04 | 0.92 |
| [CH₃[(CH₃)₂SiO]₄]₂CH₃SiO]₃Fe                                         | 0.449(2) | 0.897(3) | 0.38 | 0      | 1.64 | 0.486(5) | 0.74(1) | 25(5) | 0.18 | 0.02 | 0.92 |
| [[CH₃(CH₃)₂SiO]₄]₂CH₃SiO]₃Fe + CH₃(CH₂)₉SH (Fe:S=1:0.92)              | 0.443(3) | 0.823(5) | 0.37 | 0.01 | 1.23 | 0.415(6) | 0.86(1) | 81(5) | 0.42 | 0.05 | 0.96 |
| [[CH₃(CH₃)₂SiO]₄]₂CH₃SiO]₃Fe + CH₃(CH₂)₉SH (Fe:S=1:1,40)              | 0.448(4) | 0.746(6) | 0.37 | 0.08 | 1.27 | 0.424(6) | 0.75(1) | 82(3) | 0.45 | 0.08 | 1.00 |

Figure 1. Moessbauer spectra of four iron organosiloxanes at 77 K.
The better fit for the spectra can be obtained using two doublets. The respective results are presented in Tables 1 and in Figure 1(b-d). It is clearly seen that all the parameters of smaller doublet including relative intensity are similar for each sample. For the doublets with the larger splitting the isomer shifts are also very similar, but quadrupole splitting is decreased with the rise of the sulfur content in the sample.

Regarding the values of the isomer shifts of siloxyiron it is reasonable to take into account the known values for iron silicates. Iron has an octahedral arrangement in Ca$_3$Fe$_2$Si$_3$O$_{12}$ [5,6] with garnet structure ($\delta = 0.41 \text{ mm} \cdot \text{s}^{-1}$) and in NaFeSi$_2$O$_6$ [7,8] with the structure of pyroxene ($\delta = 0.41 \text{ mm} \cdot \text{s}^{-1}$). These values are slightly different from the isomer shifts of $\alpha$-Fe$_2$O$_3$ [9,10], which consists of regular oxygen octahedra of corundum structure ($\delta = 0.36 \text{ mm} \cdot \text{s}^{-1}$). Tetrahedral polyhedron is in KFeSi$_2$O$_6$ [11] with leucite structure ($\delta = 0.25 \text{ mm} \cdot \text{s}^{-1}$) and KFeSi$_3$O$_8$ [11,8] with pollucite structure ($\delta = 0.23 \text{ mm} \cdot \text{s}^{-1}$) *.

First, to make a comparison we have to refer our calculated isomer shifts to room temperature. In our case it is possible to apply an increment of approx. -0.1 mm/s. Now it could be seen that all calculated isomer shifts are between the above mentioned values for iron in tetrahedral and octahedral arrangements. It is possible to suggest that the coordination polyhedron of iron in our compound is distorted. Such an interpretation is correlated with Moessbauer data for \textit{C120H100Si20O43Fe6Na8}⋅9C4H9OH⋅C7H8 which contains penta- and hexacoordinated iron ($\delta = 0.33\pm0.05 \text{ mm} \cdot \text{s}^{-1}$) [12].

The treatment of [\textit{CH}_3\{\textit{CH}_3\}_2\text{SiO}]_2\{\textit{CH}_3\text{SiO}]_2\text{Fe} with 1-decanthiol can lead to substitution of $\sigma$-unbonded oxygens in iron polyhedron into sulfur. This can explain the difference in quadrupole splitting for the doublets with the larger splitting. Increase of sulfur content in the samples results in decreasing of the splitting.

What is remarkable is that doublets with smaller splitting have thin lines. The isomer shift is very close to the shift of $\alpha$-Fe$_2$O$_3$. The doublet can be related to a by-product, which can be formed during the synthesis of [\textit{CH}_3\{\textit{CH}_3\}_2\text{SiO}]_2\{\textit{CH}_3\text{SiO}]_2\text{Fe} as a result of hydrolysis of Fe-O-Si groups followed by the condensation. It is important to emphasize that this constituent remains unchanged during the treatment of the oligomer with the thiol.

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* Room-temperature isomer shifts are presented in this paragraph.