

**STRUCTURAL STUDY OF DEXTRANE, HYDROGENATED DEXTRANE,  
AND THEIR IRON(III) COMPLEXES.  
PART I. INFRARED AND ESR SPECTRA OF THE IRON(III) COMPLEX  
OF HYDROGENATED DEXTRANE**

Key words: dextrane, hydrogenated dextrane, hydrogenated dextrane iron(III)  
complex, IR spectra, ESR spectra

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**ABSTRACT**

The infrared spectra of dextrane, hydrogenated dextrane and the complex of hydrogenated dextrane with iron (III) (fedex) have been recorded in the range between 4000 and 300  $\text{cm}^{-1}$ . The infrared spectrum is consistent with C1 conformation of the glucopyranose unit in dextrane, hydrogenated dextrane and fedex. The hydrogen bonds in the structure of fedex molecule are stronger than that of the other studied compounds. The degree of branching in the glucopyranose chain is very low. The IR

spectral data indicate that in the fedex structure,  $\beta_2$ -FeOOH is probably present. The ESR spectra indicate that the coordination around the iron ion is probably octahedral.

## INTRODUCTION

Different types of iron(III) hydroxide carbohydrate complexes are of interest as suitable oral iron preparations used for the prevention and treatment of iron deficiency.<sup>1</sup> Dextrane compounds and their complexes with some metal ions have been studied extensively.<sup>1-6</sup> A variety of instrumental techniques have been used. The complexes have been characterized by gel filtration, ESR and IR measurements, Mössbauer spectroscopy, electrophoretic and polarographic investigations.

Electron resonance spectra of iron metal complexes of different carbohydrates such as polyisomaltose and polymaltose are reported. The interest of the investigators mainly being centered on type of interactions between iron clusters and the ligand species.<sup>2</sup>

The infrared studies have been focused mainly on the  $\nu(\text{OH})$  and  $\delta(\text{OH})$  vibrations of the iron(III) hydroxide and their modifications.<sup>1,5</sup>

Being interested for some time in the study of the dextrane and hydrogenated dextrane complexes with iron(III) hydroxide and continuing our work on the spectra of dextrane compounds<sup>5</sup> we decided to study the ESR and IR spectra of the title compounds. We use some characteristic carbohydrate IR frequencies in diagnosing the nature of the glycopyranose conformation unit in these compounds. With the aid of ESR measurements we have made an attempt to propose the type of coordination around the iron ions. In addition, some structural aspects of iron(III) hydroxide moiety in the fedex molecule are discussed.

**EXPERIMENTAL PART**

All studied compounds were prepared by published methods.<sup>3, 4</sup> Low molecular dextrane was obtained by depolymerisation of clinical dextrane with molecular mass 70 000 by standard procedure. Hydrogenated low molecular dextrane (HDD) was prepared with potassium borhydride at room temperature. Polinuclear complex with iron (III) was prepared by heating in alkaline media at 120 °C a mixture of iron (III) hydroxide and hydrogenated dextrane in molar ligand to metal ratio 1:3. The pure compound was obtained by preparative column gel chromatography on Sephadex G-1600 with water as mobile phase.<sup>3</sup>

The infrared spectra were recorded at room and liquid-nitrogen temperature (RT and LNT), on a Perkin-Elmer 580 infrared spectrophotometer and FT spectrophotometer Perkin-Elmer 1600. A VLT-2 cell was used for the low temperature measurements.

Electron spin resonance spectra were recorded on a Bruker 200 ESR spectrometer employing 100 KHz modulation and a nominal frequency of 9.5 GHz. Further details of the ESR measurements are given elsewhere.<sup>10</sup>

**RESULTS AND DISCUSSION**

The infrared spectra of dextrane, hydrogenated dextrane and the complex of hydrogenated dextrane with iron (III) are presented in fig. 1. As in practically all polysaccharides<sup>7</sup> and their complexes with metal ions,<sup>3-5</sup> numerous and not well-resolved bands even at liquid-nitrogen temperature are observed in their infrared spectra (fig. 1). The information which can be gained from the infrared spectra are, thus of limited value. In spite of that, some spectral information can be extracted.

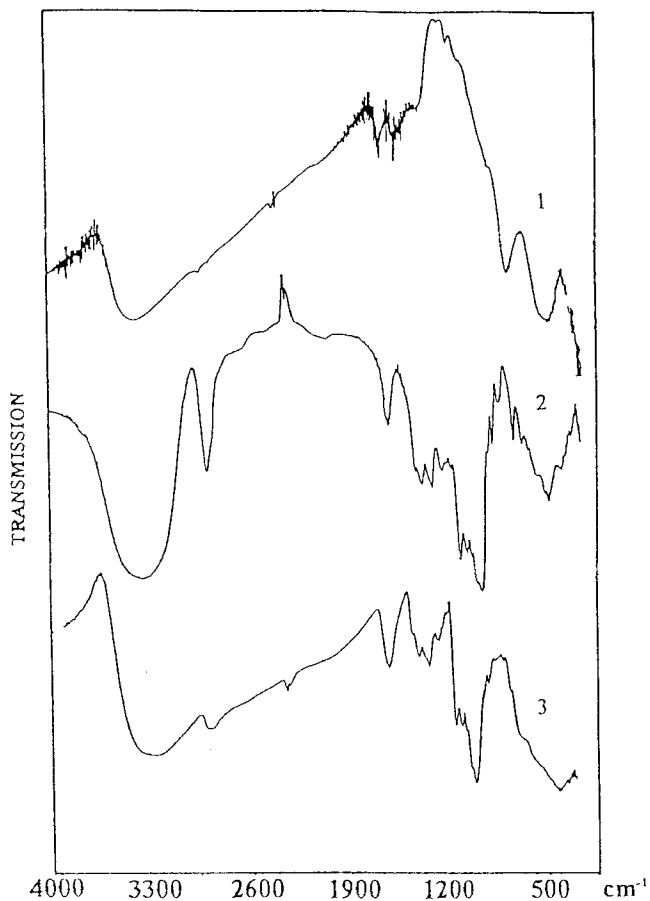


FIG. 1. Infrared spectra of 1)  $\beta_2$ -FeOOH; 2) HDD; and 3) fedex.

In the infrared spectra of all studied compounds a broad and very intensive complex feature with a main maximum between  $3400\text{ cm}^{-1}$  and  $3300\text{ cm}^{-1}$  is present. The centroid of the complex band in the spectrum of the iron complex with hydrogenated dextrane lies lower than that in the spectrum of dextrane and hydrogenated dextrane. In fact, judging from the frequencies, shape and intensities

of the OH bands, there is no doubt that the O...O hydrogen bonds in the structure of fedex molecule are stronger than that of other studied compounds.

In the region between 1200-1000  $\text{cm}^{-1}$  a complex band with several maxima at 1147, 1104, 1068, 1025 and 1007  $\text{cm}^{-1}$  is observed in the spectra of dextrane, HDD and fedex (cf. fig. 1). These bands have been commonly found in most carbohydrates and according to normal coordinate treatment<sup>11, 12</sup> have been assigned as coupled vibrations involving CO, COC, CCC and CCO antisymmetric stretches. The high frequencies at 1147 and 1104  $\text{cm}^{-1}$  in the fedex spectrum, are considered to be mainly due to antisymmetric stretching of the glycoside bridge group. The similarity of the frequencies, intensity and shape of these bands implies that in the title compounds there are no significant difference in the C-O-C glycoside linkage and degree of chain branching is probably very low.

In the spectra of HDD and fedex molecule, bands of negligible intensity are found in the region 900-800  $\text{cm}^{-1}$ . According to the normal coordinate treatment on the dextrane model consisting of 48 atoms,<sup>11</sup> these bands are interpreted as due to mixed CCH deformation vibrations coupled with C-C stretchings, and CCO, OCO, COC bendings in the glucopyranose units. In addition, an effect of change of conformation was observed, especially in the range of 700 to 1000  $\text{cm}^{-1}$ .

When glucopyranose units with C1 chair conformations are present,<sup>7</sup> the infrared spectra exhibit one band in the region between 925-885  $\text{cm}^{-1}$  and another one around 855-820  $\text{cm}^{-1}$ . In this particular region, as can be seen in fig. 2, where the corresponding bands are indicated by arrows, at least two weak bands around 900  $\text{cm}^{-1}$  and another at 840  $\text{cm}^{-1}$  are observed, which are assigned to mixed CCH deformation vibrations.

At first glance, the similarities of the CCH deformations modes indicate that there is no difference in the conformation of the glucopyranose unit in the HDD and fedex molecule and they probably exhibit C1 chair conformation.<sup>7</sup>

The strong band due to  $\delta(\text{OH})$  vibrations from the iron(III) hydroxide part of the molecule is in the region around  $700\text{ cm}^{-1}$ , but unfortunately the exact assignment is complicated by the fact that, in the same region, bands arising from the hydrogenated dextrane vibrations are present. In this particular region the spectral picture is altered probably by an intensive band due to  $\delta(\text{OH})$  vibrations from the  $\beta_2\text{-FeOOH}$ . As seen in fig. 2 (curve 3), the band arising from the O-H deformation vibration appears as a shoulder around  $700\text{ cm}^{-1}$  (cf. fig. 2) where the corresponding bands are indicated by asterisks). This spectral picture indicate that in the fedex molecule,  $\beta_2\text{-FeOOH}$  is probably present,<sup>1</sup> which is in agreement with our earlier findings from Mössbauer spectroscopy.<sup>5</sup>

A typical ESR spectrum of a fedex sample recorded at room temperature is presented in fig. 3. The most probable source of the intense resonance that is characteristic of the fedex system is  $\text{Fe}^{+3}$ . An effective  $g$  of  $2.02 \pm 0.01$  and a linewidth  $\Delta H_{p-p}$  of  $90 \pm 5\text{ mT}$  are evidence that these parameters are determined by strong magnetic interaction between paramagnetic ions.<sup>1, 8, 9</sup> Such interactions could occur in regions of fedex sample with high concentration of paramagnetic  $\text{Fe}^{+3}$ . A similar resonance has been detected in samples of muscovite, phogopite and in the ESR spectra of other carbohydrates iron(III) complexes in which the concentration of  $\text{Fe}^{+3}$  were substantial. The later resonance is attributed to the exchange interaction between clusters of  $\text{Fe}^{+3}$  ions.

The ESR spectrum can be described by a spin Hamiltonian of the following form:

$$H = g \beta \mathbf{H} \cdot \mathbf{S} + D [S_z^2 - 1/3 S(S+1)] + E (S_x^2 - S_y^2)$$

where the effective spin  $S$  for  $\text{Fe}^{+3}$  ion is  $5/2$ , and  $D$  and  $E$  energy terms

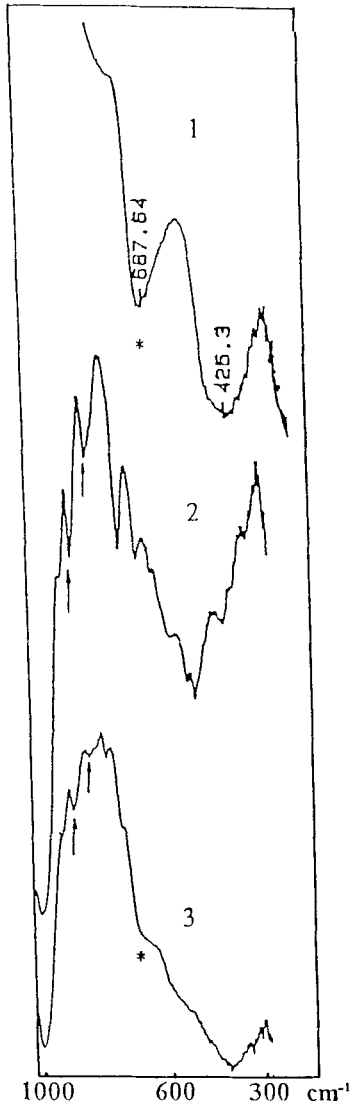


FIG. 2. Infrared spectra in the region between 1000-300 cm<sup>-1</sup> of  
1)  $\beta_2$ -FeOOH; 2) HDD; and 3) fedex.

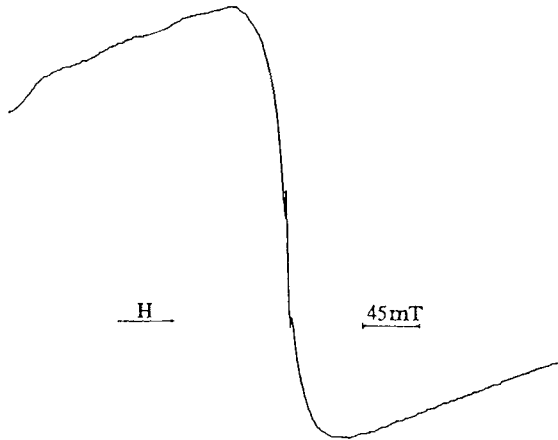


FIG. 3. ESR spectrum of fedex.

representing axial and rhombic components of the local crystal field at  $\text{Fe}^{+3}$  sites. If the  $D$  and  $E$  terms are much greater than the Zeeman term  $g\beta\mathbf{H} \cdot \mathbf{S}$ , the resonance at  $g$  would be far from the free spin value 2.0023. In the other case, if the  $D$  and  $E$  terms are very close to zero, then  $g$  approaches 2.00, as we found in the fedex ESR spectrum.

In addition, the  $g$  value for the iron complex with hydrogenated dextrane is in the range commonly found for the octahedrally bound iron ions in compounds with polyisomaltose, polymaltose and similar carbohydrates which indicate similarities in the interaction between iron ions and ligands in these compounds.<sup>2</sup>

In spite of the difficulties concerning the determinations of the bands due to iron hydroxide vibrations on the basis of the available evidence from ESR spectra and literature data, we suggest that the most probable coordination around iron ions is octahedral.



**CONCLUSIONS**

Considering the complexity of the compounds, from the IR and ESR spectra some structural informations concerning the relative strength of hydrogen bonding, the conformations of glucopyranose units, the degree of chain branching and the presence of the  $\beta_2$ -FeOOH moiety in the fedex molecule, were obtained.

From the ESR and the and IR spectra alone, we were unable to distinguish between octahedral and tetrahedral coordination around  $\text{Fe}^{+3}$  and further studies are in progress to resolve the problems about the mode of iron(III)-hydrogenated dextrane interactions. In this case, where resolution is poor, computer simulation is an imperative as a test of the spectral analysis. The spectral similarity could be correlated to the type and degree of chain branching established by methylation analysis.

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