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SYNTHESIS, MÖSSBAUER AND MAGNETIC CHARACTERIZATION OF SOME IRON(III)--NUCLEIC ACID COMPONENTS (NUCLEOTIDE, NUCLEOSIDE AND BASE)

New synthesis of iron(III)-nucleic acid components have been carried out. The characterization of these compounds has been done by means of Mössbauer and magnetic measurements, UV-Visible and infrared spectra.

The study of the different mechanisms of interactions between the central cation (Fe^{3+}) and the components of nucleic acids is of major interest in life science [1]. Therefore it is very important to relate the data obtained by using microscopic and macroscopic techniques in order to establish the correlation between physical properties and biological behaviour [2].

In this paper we show some results [3] of our research in the field of metal-DNA compounds interaction.

In Table I we list the compounds which have been studied.

Table I

Compound	Q.S. (mm/s)	I.S. (mm/s)
Fe-adenosine	0.59	0.28
Fe-citosine	0.64	0.26
Fe-hipoxantine	0.65	0.29
Fe-guanine	0.61	0.28
Fe-ATP	0.59	0.29

An aqueous solution of $FeCl_2.4H_2O$ was mixed with a nucleotide, nucleoside or base solution keeping the pH values below 6. All the complexes were precipitated by addition of EtOH, filtered and dried "in vacuo".

UV-Visible and infrared spectra were recorded for all the compounds obtained.

Mössbauer spectroscopic measurements at room temperature were registered using a conventional apparatus. The single line source used was ^{57}Co (10 mCi) in a Rh matrix.

Magnetic susceptibility measurements were made in a Faraday type balance in the temperature range 80-300 K and in fields up to 10 kG.

In Fig. 1 we show Mössbauer spectra of some of the synthetized compounds. All the spectra consist of two lines with identical intensity and width and have been interpreted in terms of the existence of a quadrupole doublet corresponding to Fe^{3+}.

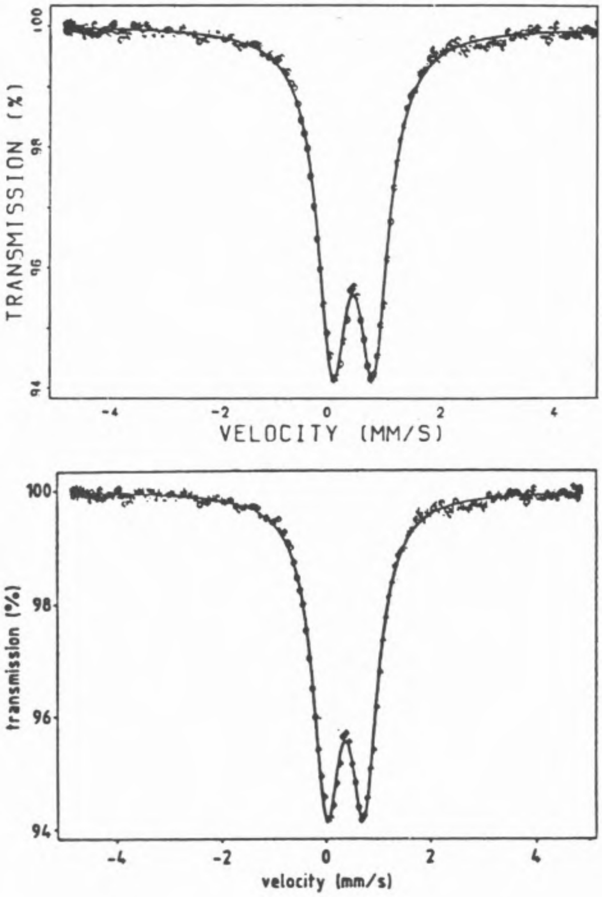

Fig. 1
Mössbauer spectra of a) Fe-Hipoxantine and b) Fe-ATP

The corrected molar susceptibilities $\chi'^{-1}_M(T)$ have been fitted in the framework of the Curie-Weiss law. The values of the atomic dipolar magnetic moments (μ) and the Curie temperatures (θ) of the different compounds have been obtained from a least squares computed fit of $\chi'^{-1}_M(T)$.

Both the isomer shift values (I.S.) and the dipolar magnetic moment values correspond to a high spin Fe(III)-$^6S_{5/2}$ configuration. The positive values of the Curie temperatures suggest that an antiferromagnetic interaction between the Fe ions in these compounds does exist.

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MAGNESIUM(II)-INDUCED EFFECTS ON THE STABILITY OF THE ADENOSIDE-THYMIDINE COMPLEX IN SOLUTION

Proton-carbon selective NOE measurements have been used to prove previously suggested conformations of model compounds [1] and biological macromolecules [2,3]. The observation of through-space selective dipolar couplings between carbon and proton atoms allowed the derivation of the intermolecular distance in solution [3,4]. In this study the observed heteronuclear NOE values have been used to monitor the presence of Adenosine-Thymidine complexes. A particular attention has been devoted to value the presence of Watson-Crick-type and Hoogsteen-type base pairing. ^1H-^{13}C heteronuclear Overhauser effects, obtained by selective perturbation of the resonance line of protons involved in hydrogen bonding, allowed the identification of intermolecular interaction patterns. These studies have been extended to monitor the effects induced on the stability of Adenosine-Thymidine complexes by the addition of magnesium ions to the solution.

Adenosine and Thymidine were obtained from Sigma Chemical Co., both nucleosides having been dissolved in 99.98% DMSO-d_6 to yield 0.5 M solutions. $Mg(ClO_4)_2$ (Merck) 0.25 M was used as the source of magnesium ions. All NMR measurements were made on a Varian XL-200 spectrometer. The temperature was held constant at 40°C. The nuclear Overhauser effect, which occurs whenever spectra are recorded under conditions of continuous broad-band proton decoupling (BB), causes intensity enhancements of carbon resonances. The observed NOEs are related to the relaxation parameters by the following equation:

$$NOE_{13_C}(BB) = (I_z - I_o)/I_o = \frac{\gamma_H}{\gamma_C}\,\frac{\Sigma\sigma_i}{R_C} \qquad (1)$$

where γ are the magnetogyric ratios, I_z and I_o are peak intensities measured under continuous and gated decoupling conditions, R_C is the spin-lattice relaxation rate of the proton decoupled carbon resonance and σ_i are the cross-relaxation contributions which occur between carbon and proton nuclei.

Upon selective saturation of a proton H_a which dipolarly interacts with a ^{13}C nucleus C_b, at a distance r_{ab}, the $NOE_{13_{C_b}}(H_a)$ can be described by the equation:

$$NOE_{13_{C_b}}(H_a) = \qquad (2)$$
$$= \frac{1}{R_{13_C}}\,\frac{\hbar^2\gamma_H^3\gamma_C}{10\, r^6_{C\text{-}H_a}}\left[\frac{6\tau_c}{1+(\omega_H+\omega_c)^2\tau_c^2} - \frac{\tau_c}{1+(\omega_H-\omega_c)^2\tau_c^2}\right]$$