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METAL ION — AND VITAMIN B_6 — CATALIZED TRANSAMINATION AND DEPHOSPHONYLATION OF 2-AMINO-3-PHOSPHONOPROPIONIC ACID

Kinetic studies have been carried out for reactions of Schiff bases (SB) formed from pyridoxal 5'-phosphate (PLP) and 2-amino-3-phosphonopropionic acid (APP): 1:1:x Zn(II)-SB-PDA system where PDA is 2,6-pyridinedicarboxylic acid; 1:2 Ga(III)-SB system; and 1:2 Al(III)-SB system). Formation and disappearance of a ketimine intermediate and its complexes were followed by proton NMR and ^{31}P NMR. The reaction occurs in two distinct sequential steps: transamination and dephosphonylation. The specific rate constants for individual species of the metal-free systems are: $k_{H_4SB} = 1.64 \times 10^{-4}$ s^{-1}, $k_{H_3SB} = 7.56 \times 10^{-5}$ s^{-1}, and $k_{H_2SB} = 2.34 \times 10^{-5}$ s^{-1} for the transamination step. The values for k_{HSB} and k_{SB} are about zero. The corresponding dephosphonylation rate constants $k'_{H_4SB} = 4.27 \times 10^{-6}$ s^{-1}, $k'_{H_3SB} = 1.26 \times 10^{-6}$ s^{-1} and $k'_{H_2SB} = 6.84 \times 10^{-7}$ s^{-1} were determined for the dephosphonylation step. The values for k'_{HSB} and k'_{SB} are about zero. Transamination and dephosphonylation proceed more rapidly for the Ga(III) complexes than for those of Al(III) and Zn(II). The specific rate constants in the transamination step for the individual species of 1:2 Ga(III)-SB system are: $k_{Ga(H_3SB)_2} = 4.66 \times 10^{-4}$ s^{-1}, $k_{GaH_5(SB)_2} = 3.51 \times 10^{-4}$ s^{-1}; $k_{Ga(H_2SB)_2} = 3.13 \times 10^{-4}$ s^{-1} and $k_{Ga(SB)_2} = 3.12 \times 10^{-5}$ s^{-1}. The specific rate constants for the dephosphonylation step are: $k'_{GaH_5(SB)_2} = 5.2 \times 10^{-6}$ s^{-1}; $k_{Ga(H_2SB)_2} = 5.20 \times 10^{-6}$ s^{-1}; $k_{GaH_3(SB)_2} = 5.17 \times 10^{-6}$ s^{-1}; $k_{Ga(HSB)_2} = 5.09 \times 10^{-6}$ s^{-1}; $k_{GaH(SB)_2} = 2.53 \times 10^{-6}$ s^{-1} and $k_{Ga(SB)_2} = 4.92 \times 10^{-7}$ s^{-1}. The results show that the most active species are those in which the carboxylate group of the amino acid moiety of the SB ligand is coordinated to the metal ion and the phosphonate is not coordinated.

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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+}.

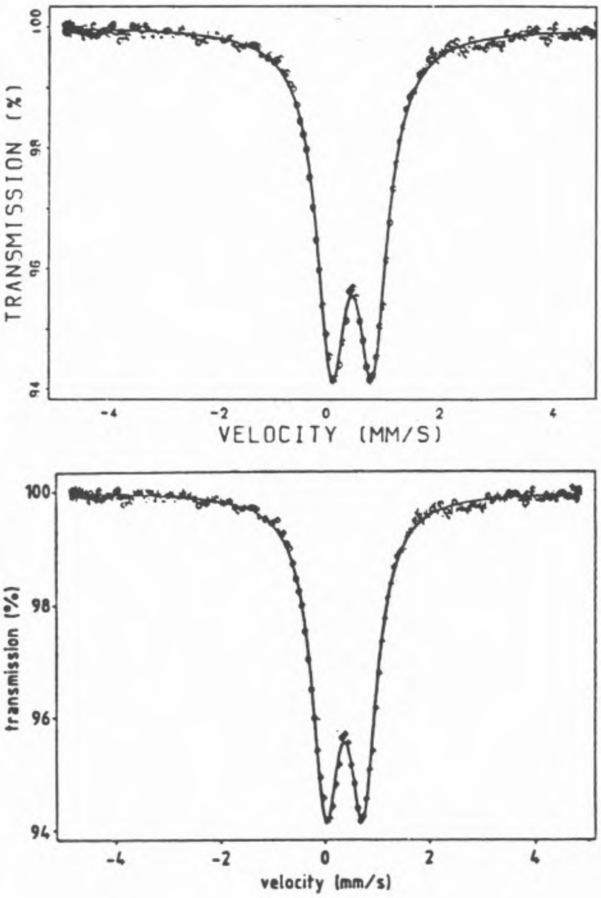

Fig. 1
Mössbauer spectra of a) Fe-Hipoxantine and b) Fe-ATP