

NMR method These investigations made it possible to determine the coordination mode of aminoacids with lanthanide ions The results are also of biological interest, since the lanthanides are often used as probes in calcium biochemistry From our earlier studies on interaction of La(III), Lu(III) and Nd(III) ions with aspartic acid and asparagine it follows that light and heavy lanthanide ions interact in different ways with the carboxylic groups of aminoacids In order to confirm this suggestion we extended our studies to glutamic acid and γ carboxyglutamic acid ^1H , ^{13}C NMR and electron spectra were recorded Correlation of NMR chemical shifts with hypersensitive band intensity changes of lanthanide ions allows the determination of the coordination mode of the discussed aminoacids Obtained results were confirmed by the Eu(III) luminescence spectra

Conformational and Dynamic Aspects of an Ion Binding Cyclic Peptide Analogue of Valinomycin, Cyclo(LAla-Gly DPhe LPro)₃

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We have investigated the binding of various cations Ba, K, Rb, Cs, Na and Li to a newly synthesized cyclododecapeptide cyclo (LAla Gly DPhe LPro)₃ in various solvents by using the Nuclear Magnetic Resonance technique

It was shown that Na and Li form primarily 1/2 ion peptide complexes with the cyclic peptide while the other cations form mainly 1/1 ion peptide complexes

Temperature variation and solvent perturbation techniques were used in addition to the coupling constants to deduce the conformations of the 1/1 ion peptide complexes These were found to be related to the bracelet conformation of the valinomycin K complex However, small but significant conformational differences were found in the various cation complexes which could be explained on the basis of the cation characteristics

Isotope exchange studies also allowed us to propose a mechanism of cation release capture involving the breaking of three of the six intramolecular hydrogen bonds which stabilise the 1/1 ion peptide complex

NMR Study of Interaction of Nucleic Acid Bases in DMSO

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The mechanism of the interaction of DNA bases, with DMSO, or with other solutes in DMSO is not clear It was suggested that this interaction might be through the formation of hydrogen bonding or through charge transfer complex [1]

The aim of this work is to study the interaction of those bases with different acceptors such as nitromethane, nitrobenzene, acetyl acetone, nicotine and acridon, using NMR techniques, in hope of shedding some light on the nature of the above mentioned interaction

Uracil

At low concentrations (0.06 M) N₁H signal did not separate from N₃H, this is a good indication that uracil association is stronger than uracil-DMSO However when a fixed concentration of uracil is mixed with varying concentration of acetyl acetone, acridon, nicotine and nitromethane, N₁H separates from N₃H and proton 5 splits into a doublet of doublets with $^4J_{\text{N}_3\text{H H}_5} = 1.5 \text{ Hz}$ [2] This indicates that N₃H freezes before N₁H due to the formation of hydrogen bonding between the more acidic proton (N₃H) and the above mentioned acceptors All these acceptors seem to form similar types of hydrogen bonds with uracil

Thymine

Dilution of thymine with DMSO will cause N₁H signal to separate from N₃H, this proves that thymine-thymine interaction is weaker than thymine-DMSO interaction Addition of a small amount of the acceptors to thymine causes N₁H to separate from N₃H, one could conclude that uracil-uracil association is much stronger than thymine-thymine

Cytosine

This study did not obtain any indication of the formation of tautomer in DMSO as reported before [3] All acceptors didn't cause any effect on cytosine except for nitromethane, such that when the ratio of nitromethane cytosine was 5:1, a broad band appears at about 10-11 ppm and protons 5 and 6 split to a doublet of doublets with $J = 2.0 \text{ Hz}$ This could be explained, that cytosine exists in the tautomer form [4], which might be stable in nitromethane medium, one could conclude that the coupling observed is between N₃H and protons 5 and 6 [5]