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. ^{1}H, ^{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) luminiscence spectra.

Conformational and Dynamic Aspects of an Ion-Binding Cyclic Peptide Analogue of Valinomycine, 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*) N_1H signal did not separate from N_3H, 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, N_1H separates from N_3H and proton 5 splits into a doublet of doublets with $^{4}J_{N_3H,H_5} = 1.5$ Hz [2]. This indicates that N_3H freezed before N_1H due to the formation of hydrogen bonding between the more acidic proton (N_3H) 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 N_1H signal to separate from N_3H, this prove that thymine–thymine interaction is weaker than thymine–DMSO interaction. Addition of a small amount of the acceptors to thymine cause N_1H to separate from N_3H, 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 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 N_3H and protons 5 and 6 [5].

Purine

It was suggested that with increasing concentration purine associates through stack formation [6]. Hewson *et al.* [7], concluded that purine associates through hydrogen bonding. In this work we noticed that there is no change in the chemical shift of proton 2, 6 and 8, but N_9H moves to higher field with increasing concentration. It seems that purine associates in a manner similar to that in pyrrol [8]. No change was observed with all acceptors except with acetyl acetone and acridon where N_9H shifted to low field upon the mixing of purine with those two acceptors, this is strong evidence for the formation of hydrogen bonding between purine and each of acetyl acetone and acridon.

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Evidence for Different Types of Interaction between Anions and the Copper(II) Site of Superoxide Dismutase

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It seems now well established that the two equivalent copper(II) ions in dimeric superoxide dismutase are exposed to solvent as well as to solute molecules, while the two zinc(II) ions are not capable of such interactions [1–4]. Water proton relaxation studies [5] have shown that anions bind the copper atom by displacing the coordinated water molecule; the obtained affinity constants roughly compare with those calculated through inhibition measurements [5], suggesting the identity between the water and the inhibitor binding sites.

The present report aims to show evidence for a second copper binding site for anions, not involving displacement of water; this site may also be of importance for the catalytic process.

Previous investigations have shown that the thiocyanate ion is able to affect the ESR spectra of copper(II) in superoxide dismutase [6], whereas it has been subsequently shown not to affect the catalytic activity. Therefore, a detailed study of the interaction between the above ion and superoxide dismutase has been undertaken, by means of electronic, ESR, and ^1H and ^{13}C NMR spectroscopy.

While the electronic spectra of the copper chromophore as well as the water proton relaxation of enzyme solutions remain substantially unchanged up to 0.5 *M* KNCS concentrations, the ESR parameters and the ^{13}C relaxation times of the anion are significantly affected. In particular, the ^{13}C signal of NCS^- dramatically broadens, consistently with a direct binding to the paramagnetic metal ion. From the dependence of the paramagnetic effect on the thiocyanate concentration an affinity constant of 50 ± 10 M^{-1} can be estimated. The ESR data on frozen solutions qualitatively agree with the above value, as judged from the progressive variation of A from 145 to 160 $cm^{-1} \times 10^4$ upon anion addition.

By increasing the thiocyanate concentration above 1 *M* a further range is observed in the ESR spectra, which show a *decrease* in the A value; a slight blue shift is observed in the electronic spectra and the water proton relaxation is reduced. Limit values of the above parameters could not be obtained; the affinity constant can be estimated to be in the range $0.1–1\ M^{-1}$.

All of the above results strongly suggest the existence of a second, non inhibitory anion binding site on copper in superoxide dismutase which, in the case of the thiocyanate anion, is preferred to the site of water. The electronic and ESR spectra of the adducts indicate that there are not major variations in the coordination geometry of the copper chromophore, which seems to be more consistent with the detachment of one of the four inplane imidazole donors that with the addition of the thiocyanate ion to a sixth coordination position.

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