nucleic acid interactions are also investigated. The 5'ATP–Mn(II)–*apo*BCA system has been studied under different experimental conditions. The EPR lineshape has been analyzed in terms of a relaxation model based on a distribution of ZFS sites. Typical inverted spectra have been found whenever ternary interaction occurred (Fig. 1). Paramagnetic contributions of T_{1p}^{-1} and T_{2p}^{-1} to ^{13}C and ^{1}H relaxation rates were investigated by taking into account a distribution of correlation times and the competition between τ_r and τ_s connected with the formation of ternary species.

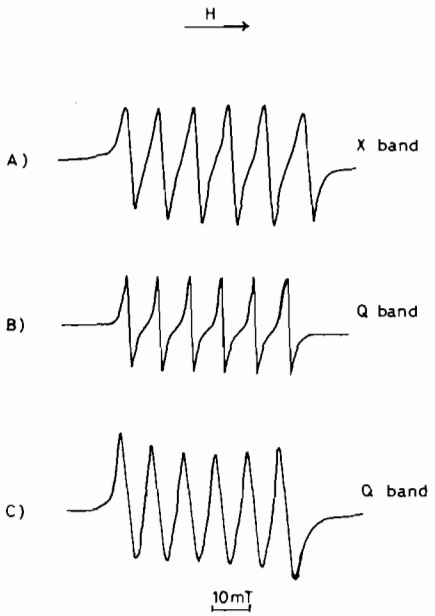

Fig. 1. A) X-band (ω = $5.8 \cdot 10^{10}$ rad/sec) and B) Q-band (ω = $2.16 \cdot 10^{11}$ rad/sec) experimental EPR spectra of aqueous solutions of Mn(II) [$2.5 \cdot 10^{-3}$ *M*] and *apo*-BCA [$2.5 \cdot 10^{-4}$ *M*]. C) Q-band EPR spectrum of the 5'-ATP–Mn(II)–*apo*-BCA ternary system. [5'-ATP] = $2.5 \cdot 10^{-2}$ *M* at pH = 7 and T° = 300 K.

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Conformational Effects of the Solvent Media on Oligo-Peptides

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For large peptides of biological interest it seems reasonable that the molecules could have a fairly well defined three-dimensional structure in solution, but considering the smaller oligopeptides it is of interest to ask if these molecules also exist in a preferred conformation in solution [1].

It has often been assumed that oligopeptides in solution could form intramolecular hydrogen bonds giving rise to several types of bends (β turns, γ turns, seven membered rings...) which stabilize the preferred conformations. This ability seems to be related to the nature of the amino acidic residues and to the solute–solute–solvent interactions. For example the hormonal peptide oxitocin and related peptides present different conformational features in DMSO and in water [2]. This behaviour seems to be quite general and we have undertaken CD and NMR studies to elucidate the actual stereochemistry of some model oligopeptides (HCl·Leu-Gly-OEt, Boc-Leu-Gly-OEt, Boc-Pro-Leu-Gly-OEt, Boc-Ile-Pro-Leu-Gly-OEt, Boc-Ala-Pro-Leu-Gly-OEt, Z-Gly-Pro-Leu-Gly-OEt, (Boc-, Z-,)-Cys-Pro-Leu-Gly-OEt) and to evaluate the role of the single aminoacid residue and the importance of environmental situations when these oligopeptides are allowed to assume preferred conformations.

Both CD and NMR (^{1}H and ^{13}C) clearly indicate that the ability to form stabilizing intramolecular hydrogen bonds does not depend on the amino acidic residues, but the polarity of the solvent plays the more relevant role. Infact the less polar media can induce intramolecular interactions whose existence cannot be detected in more polar media.

Moreover the same phenomenon occurs also in the case of the smaller peptides where the protecting groups became involved in the same type of intramolecular interactions.

However increasing the concentration of the oligopeptides in the solvents phenomena of intermolecular association begin to take place and the intramolecular interactions are no longer observable.

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