biomolecule interactions have been analyzed and experimental data suggest that solvent exposed amide groups are hydrogen bonded with nitroxide N-oxyl moieties. This interaction and random biomolecule–nitroxide collisions determine the extent of observed paramagnetic effects on proton relaxation rates. Dipolar relaxation occurs between the unpaired electron of the nitroxide and proton nuclei of the biomolecule, but a quantitation of relaxation enhancements in terms of exposure factors is not straightforward, due to the complexity of biosystems where many simultaneous interacting sites have to be taken into account. Nevertheless, a qualitative insight into solvent accessibility to protons attached to complex molecular systems and the conformation of their diamagnetic metal complexes is possible.

Relaxation data obtained for the 2,2,6,6-tetramethyl piperidine-1-oxyl/gramicidine S system in DMSO, shown in Table I, confirm that hydrogen bonded and/or solvent shielded protons have the smallest molar paramagnetic relaxation S_{1p}.

TABLE I. Relaxation Data.

	ppm[a]	S_{1p} (sec^{-1} M^{-1})
Leu NH	8.31	100 ± 6
Leu H	4.64	107 ± 7
Orn NH	8.62	380 ± 13
Orn H	4.94	40 ± 10
Phe NH	9.11	350 ± 15
Phe H	4.47	235 ± 10
Pro H	4.42	130 ± 6
Methyls	1.04	370 ± 14
Aromatics	7.20	410 ± 16

[a]ppm from internal TMS.

1 N. Niccolai, G. Valensin, C. Rossi and W. A. Gibbons, *J. Am. Chem. Soc., 104*, 1534 (1982).

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Application of Luminescence and Absorption Spectroscopy and the X-ray Method to the Study of Ln^{3+} Ions Interaction with Aminoacids

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Lanthanide ions have found increasing use as metal ion probes for spectroscopically inert Ca(II), and substitution of Ln(III) for Ca(II) enables the performance of absorption, luminescence and magnetic resonance studies on systems of biological interest.

In peptide and protein complexes, the Ca(II) ion is normally bound by aspartate and glutamate residues so it is crucial to the full understanding of Ln(III) binding by these materials.

In our previous papers we have examined the interaction of lanthanide ions with L-asparagine, L-glutamine, L-aspartic and L-glutamic acid in aqueous solutions. We have suggested the appearance of the dimeric forms in the latter case [1–4]. Now we report the results of our spectroscopic studies of the crystals of the Nd, Ho and Eu compounds with glycine and L-glutamic acid in solid state and of the X-ray investigations of the $[Nd(gly)_3][ClO_4]_3 \cdot 5H_2O$ crystal.

Several lanthanide ion complexes with glycine and L-glutamic acid were synthetized and yield in the form of monocrystals. Absorption spectra of the crystals were measured on a Cary 14 spectrophotometer at room temperature and 5 K. Luminescence spectra of Eu(III) and Nd(III) compounds were recorded at the same temperature. E_1 and E_2 selective excitation energies of the Nd(III) ion level revealed that the Nd(III) ion could appear in two different symmetry positions in the complexes with glutamic acid. From the measured absorption spectra the oscillator strengths of f–f transitions were estimated. The relation between f–f transition intensity and position of the crystallographic axis of crystals has been stated.

The f–f transitions were analysed on the basis of the Judd theory taking the dependence of intensity on the crystallographic axis position into account.

Intensity analysis of f–f transitions revealed quite a considerable difference in the intensity distribution of bands, especially for hypersensitive transitions. Drastic differences in Judd parameters have been found (Table I).

TABLE I. The τ_λ Parameters Values.

Compound		$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
$[Nd(Gly)_3] \cdot [ClO_4]_3 \cdot 5H_2O$	*a*	3.65 ± 0.85	5.48 ± 0.78	11.49 ± 1.10
	b	3.25 ± 0.68	5.67 ± 0.63	10.70 ± 0.88
	c	1.83 ± 0.93	6.17 ± 0.86	10.40 ± 1.20
	a (mean)	2.83 ± 0.76	5.92 ± 0.71	10.80 ± 0.99
$[Nd(Glu)][ClO_4]_2 \cdot 7H_2O$		4.72 ± 0.73	5.44 ± 0.68	12.44 ± 0.95

The crystal structure data determined by us for $[Nd(Gly)_3][ClO_4]_3 \cdot 5H_2O$ compound with space group P1, Z = 4, symmetry for Nd^{+3}; I-1 and C.N. = 9 (Fig. 1) confirm our suggestion that in lanthanide

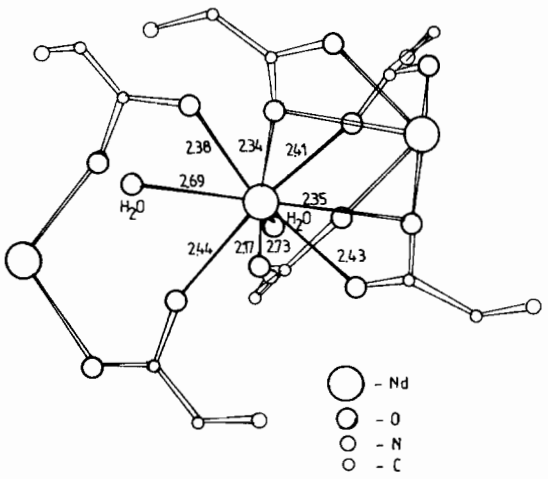

Fig. 1. X-ray structure of $[Nd(Gly)_3][ClO_4]_3 \cdot 5H_2O$.

ion complexes with aminoacids dimeric and polymeric structures may be observed.

1 J. Legendziewicz, H. Kozłowski and E. Burzała, *Inorg. Nucl. Chem. Letters, 14*, 409 (1978).
2 J. Legendziewicz, H. Kozłowski, B. Trzebiatowska and E. Huskowska, *Inorg. Nucl. Chem. Letters, 15*, 349 (1979); *ibid., 17*, 57 (1981).
3 J. Legendziewicz, E. Huskowska, W. Strek and B. Trzebiatowska, *J. of Luminescence, 24/25*, 819 (1981).

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Cu(II) as a Probe in Protein Chemistry-Binding Sites of Cu(II) in Collagen as Investigated by EPR and Electronic Spectroscopies

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Several authors [1] have found a correlation between the copper content of plasma and a chronic disease of the connective tissue usually known as rheumatoid arthritis. The copper present in the plasma is distributed between two types of complexes, labile and stable bonded ones respectively. Arthritis diseases seem to be associated with an increase in the concentration of the stably linked copper. On this basis one can surmise that some copper must be present within tendon or muscles.

In this framework we have taken into consideration the interactions of copper(II) with collagen as the major protein constituent of the tendon. The techniques used for these studies were EPR and Electronic Spectroscopy. The copper(II) is well known as a very good probe to perform EPR and electronic structural investigations on the natural and artificial copper proteins [2]. As part of our work on the protein-metal ions interactions we have examined the collagen–Cu(II) complexes (molar ratio 1:1) in the pH range 3.1–13.0.

Soluble rat collagen was obtained according to the Gallop method [3]. The analysis of the EPR spectra of freeze-dried compounds below pH = 5.4 shows the presence of the hyperfine and superhyperfine structures which are evidence for the coordination of Cu(II) to collagen at acid pH. In particular the three nitrogen superhyperfine lines suggest the one nitrogen coordination. In the pH range 5.4–10.0, collagen–Cu(II) complexes were isolated as gels, while in the pH interval 11.0–13.0 we have freeze-dried compounds. The EPR parameters of these complexes are reported in Table I: $g_{//}$ varies from 2.32 to 2.16 and $A_{//}$ varies from 140 gauss to 210 gauss. We further notice the dominance of one type

TABLE I. EPR Parameters of Collagen–Cu(II) Complexes, at 77 K.

pH	$g_{//}$	$A_{//}$
5.4	2.32	140
6.6	2.28	160
7.2	2.25	180
8.8	2.26	180
9.6	2.25	180
10.0	2.25	180
12.1	2.25	180
	2.18	200
13.0	2.16	210

of collagen–Cu(II) complex at each pH value. Hyperfine and superhyperfine structures appear in the whole pH range; specifically at pH = 12.0 nine nitrogen superhyperfine lines (A_N = 15 gauss), agree with copper coordination to four nitrogen. The EPR results are supported by further electronic spectroscopical investigations, which shows the existence of two d–d transitions, one at $\bar{\nu}$ = 12000 cm^{-1} and the other one in the $\bar{\nu}$ interval 15000–19000 cm^{-1}. Oxygenated complexes are dominant at lower pH ($\bar{\nu}$ = 12000 cm^{-1}) while with increasing pH nitrogen sites become available and progressively replace oxygenated ligands at the highest pH ($\bar{\nu}$ = 19000 cm^{-1}). Such behaviour closely resembles that observed for Cu(II)-oligopeptide models [4] and Cu(II)-β-lactoglobulin [5] complexes. However the presence of a Cu(II)–collagen complex with $g_{//}$ = 2.18 and $A_{//}$ = 200 gauss can be observed at higher pH with respect to the sequence: oligopeptides, insulin [6], β-lactoglobulin. Therefore we can suppose that nitrogen peptides become available for Cu(II)