The IR νC=O band in the free ligand (1700 cm^{-1}) suffers down shift upon complexation (1660 cm^{-1}) supporting the coordination of the Cu(II) ion through the carboxylic oxygen atom. The position of this carbonyl absorption is characteristic of a copper carboxylate species [4].

The electronic spectrum exhibits a broad band (λ = 725 nm, ϵ = 175 $l \cdot mol^{-1} \cdot cm^{-1}$), similar to those observed in copper carboxylate dimers [4]. In pyridin solution, the shift of this absorption and its higher intensity (λ = 660 nm, ϵ = 280 $l \cdot mol^{-1} \cdot cm^{-1}$) indicate the dissociation of the dimer into a monomer.

The ESR spectrum of the polycrystalline sample confirms the dinuclear character of the copper(II) complex. This spectrum consists of a copper(II) dimer typical signal with a large dipolar splitting (D = 0.3 cm^{-1}) and lines expressing spin interactions between nitroxides or between nitroxides and copper-(II) in monomeric species impurities (g = 2.025). The EPR spectrum of the compound in solution indicates the complex is dimeric in DMF and monomeric in pyridin. For the monomeric species, in pyridin, the average line characteristic of the copper nitroxide interaction is observed at g = 2.025 [5].

The magnetic susceptibility measurements, in the range 300–4 K, show an antiferromagnetic interaction between both copper ions which is similar to that of the copper acetate dimer [4]. A fitting procedure of a theoretical equation based on the isotropic HDvV-Model leads to a very good agreement between calculated and experimental susceptibilities. The following values were obtained: $J_{Cu-Cu} = -133$ cm^{-1}, $J_{\dot{N}O-\dot{N}O} = -1.9$ cm^{-1}, $g_{Cu} = 2.25$, $g_{NO} = 2.01$, x = 4.7% (monomeric impurities).

The results obtained for this complex encourage new investigations with model systems including more complex biomolecules. Selective spin-labeling of macromolecules would be helpful to obtain information on structural and dynamic aspects in biological systems (calculation of distances between paramagnetic centers, biodisponibility of a metal).

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Complexation of Sulfur Containing Aminoacids and Peptides with Metal Ions

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Because of the involvement in many bioinorganic systems, the interaction of Pd^{2+} and Hg^{2+} with some small models containing sulfur was investigated.

Complexes of aminoacids such as S-methyl cysteine and S-benzyl cysteine and dipeptides such as glycyl-S-methyl cysteine, glycyl-S-benzyl cysteine, S-methyl cysteyl-glycine and S-methyl cysteyl-S-methyl cysteine with Pd^{2+} and Hg^{2+} were studied by NMR. Further studies with Pd^{2+} were also carried out by CD.

S-methyl and S-benzyl cysteine residues in dipeptide ligands behave like simple aminoacids when bound to Pd^{2+}. The binding involves (N, S) donor set creating a new chirality center on the thioether-sulfur atom. The presence of a vicinal amino acid plays an important role in the conformation of the S-methyl cysteine and S-benzyl cysteine chelate ring and changes the kinetics of the sulfur inversion.

The ^1H NMR and CD spectra as well as consideration of molecular models were used to suggest the absolute configuration of the respective diastereomers. The S substituent was found to have a critical influence on the absolute configuration of the sulfur atom.

The formation of the metal thioether bond gives rise to several transitions in the UV region of the CD spectra where the S–Pd^{2+} charge transfer as well as intrasulfur transition can be clearly observed. In the case of Hg^{2+}, the NMR spectra show the presence of several species depending on the peptide–metal molar ratio. In acidic medium, the sulfur atom binds Hg^{2+} leading to mono- and bis-complexes. Studies have also been carried out to investigate the influence of the substituent on the sulfur atom as well as the presence of a vicinal aminoacid on the structure of the complexes.