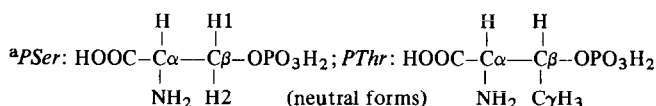


TABLE II. Calculated Electronic Charges $Q_{C,H}$ of P Ser and P Thr (Electro-Charges of Ser and Thr Are Taken from ref. 4) from H and C-13 Shifts.^a

$Q_{C,H}$	Acid		Neutral				Basic	
			(AA) _n	(AA) [±]	(AA) _n	(AA) [±]		
	Ser	P Ser	Ser	Ser	P Ser	P Ser	Ser	P Ser
$Q_{C\alpha}$	0.072	0.072	0.060	0.063	0.062	0.063	0.054	0.058
$Q_{C\beta}$	0.046	0.034	0.040	0.045	0.031	0.034	0.039	0.018
$Q_{H\alpha}$	0.054	0.055	0.048	0.053	0.053	0.053	0.047	0.049
$Q_{H\beta}$	0.054	0.058	0.053	0.054	0.057	0.056	0.050	0.055
	Thr	P Thr	Thr	Thr	P Thr	P Thr	Thr	P Thr
$Q_{C\alpha}$	0.068	0.052	0.057	0.061	0.065	0.064	0.052	0.073
$Q_{C\beta}$	0.095	0.106	0.088	0.094	0.103	0.101	0.088	0.112
$Q_{C\gamma}$	-0.106	-0.107	-0.107	-0.106	-0.108	-0.108	-0.107	-0.109
$Q_{H\alpha}$	0.053	0.054	0.047	0.053	0.049	0.049	0.046	0.045
$Q_{H\beta}$	0.050	0.056	0.050	0.051	0.053	0.053	0.050	0.049
$Q_{H\gamma}$	0.041	0.042	0.041	0.041	0.042	0.042	0.041	0.041



- G. Del Re, B. Pullman and T. Yonezawa, *Biochem. Biophys. Acta*, 75, 153 (1962).
- R. Deslauriers and I. C. P. Smith, 'Topics in Carbon-13 Spectroscopy', ed. G. Levy, vol. II, 2 (1975).
- W. J. Horsley and H. Sternlicht, *J. Am. Chem. Soc.*, 90, 3738 (1968).

U11

Paramagnetic Biomolecule–Metal Interactions: A New Dimeric Complex of Copper(II) with Spin-Labeled Glycin: Synthesis, Spectral and Magnetic Properties

COLETTE BLAQUIERE, FRANCOISE NEPVEU, MICHEL MASSOL

Laboratoire de Chimie Bioinorganique, Université Paul Sabatier, 38, rue des 36 Ponts, 31400 Toulouse, France

LEONHARD WALZ, HARALD ASTHEIMER and WOLFGANG HAASE

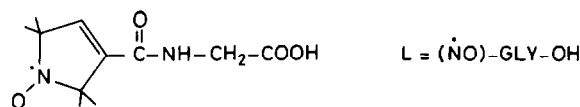
Technische Hochschule Darmstadt, Physikalische Chemie 1, Petersenstrasse 20, D-6100 Darmstadt, F.R.G.

The use of spin-label and spin-probe techniques is of considerable interest in Biology and Biophysics [1, 2]. The presence of different paramagnetic centers in biological systems, as nitroxide radicals and paramagnetic metals, and the resulting spin-spin interactions provide substantial structural and dynamic information on such systems. Studies of

model systems containing a metal ion and a labeled biomolecule by application of ESR and magnetic methods are rare. Our investigations concern a new dimeric copper(II) complex with spin-labeled glycine. We report the synthesis, spectral and magnetic properties of this complex.

Experimental

Spin labeling of glycine was performed using ethyl ester glycine and 3,5-dibromo-4-oxo-2,2,6,6-tetramethyl-piperidin-1-oxide according to the method previously described by B. T. Golding [3]. Hydrolysis of this peptidic compound with an original protocol, resulted in a new paramagnetic N-substituted α -amino-acid:



The complex was prepared by adding copper acetate monohydrate to an ethanolic solution of the labeled ligand in the ratio $\text{Cu}/\text{L} = 1/2$. The green compound was purified by recrystallization in boiling water.

Results and Discussion

Elemental analysis shows a Cu/L ratio of 1/2 and the molecular weight determined by mass spectrometry is 1142.14. These results are in agreement with a dinuclear species: $[\text{Cu}(\text{NO})\text{GLY}-\text{O}]_2 \cdot 3\text{H}_2\text{O}$.

The IR $\nu_{\text{C=O}}$ 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 ($\lambda = 725\text{ nm}$, $\epsilon = 175\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), similar to those observed in copper carboxylate dimers [4]. In pyridin solution, the shift of this absorption and its higher intensity ($\lambda = 660\text{ nm}$, $\epsilon = 280\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) 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 ($D = 0.3\text{ cm}^{-1}$) 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: $J_{\text{Cu-Cu}} = -133\text{ cm}^{-1}$, $J_{\text{NO-NO}} = -1.9\text{ cm}^{-1}$, $g_{\text{Cu}} = 2.25$, $g_{\text{NO}} = 2.01$, $x = 4.7\%$ (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).

- 1 L. J. Berliner, Ed., 'Spin labeling, theory and applications', Academic Press, Inc., New York, 1976.
- 2 G. R. Eaton and S. S. Eaton, *Coord. Chem. Rev.*, **26**, 207 (1978).
- 3 N. W. Alcock, B. T. Golding, P. V. Ioannou and J. F. Sawyer, *Tetrahedron*, **33**, 2969 (1977).
- 4 M. Melnik, *Coord. Chem. Rev.*, **36**, 1 (1981).
- 5 D. L. Dalal, S. S. Eaton and G. R. Eaton, *J. Magn. Res.*, **42**, 277 (1981).

U12

Complexation of Sulfur Containing Aminoacids and Peptides with Metal Ions

B. DECOCK-LE REVEREND, J. L. DELARUELLE, C. LOUCHEUX

Laboratoire de Chimie Macromoléculaire, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cedex, France

T. KOWALIK and H. KOZŁOWSKI

Institute of Chemistry, University of Wrocław, Joliot Curie 14, 50.383 Wrocław, Poland

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 cysteeyl-glycine and S-methyl cysteeyl-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.