Coordination isomers of histidylglycine copper(II)complex investigated by temperature dependent CW-ESR and CD spectra.

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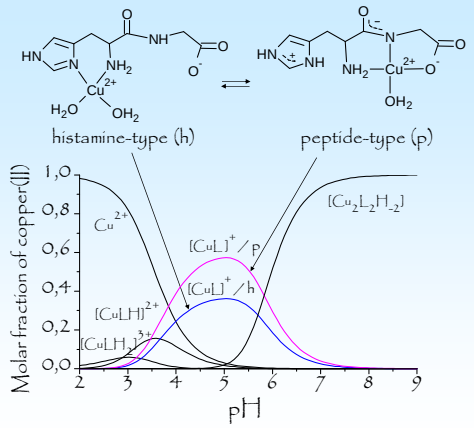
1. Introduction

The side-chain and backbone donor atoms of peptides are frequently in competition for the binding sites of metal ions. In aqueous solution of histidylglycine (HG) and copper(II) the coexistence of peptide (p) - and histamine (h) - type coordination have already been detected for the complex $[CuL]^+$ by ESR method [1]. In this work our goal was to give further evidence for the existence of these coordination isomers and determine the thermodynamic parameters of this equilibrium by the help of temperature dependent CW-ESR and CD methods. As a comparison, temperature dependent ESR spectra were recorded for the [CuLH-1] complex of glycylglycine (GG) in which peptide-type coordination can only occur.

1. T. Szabó-Plánka, N. V. Nagy, A. Rockenbauer and L. Korecz, *Inorg. Chem.* 2002, 41, 3483-3490



Distribution of copper(II) – HG species and the structure of $[CuL]^+$ coordination isomers.

2. Experimental

ESR and CD spectra were recorded between 283 – 328 K in steps of 5 K at pH=5.05 in the equimolar solution of copper(II) and histidylglycine (c = 5mM). ESR spectra were recorded with a BRUKER EleXsys E500 spectrometer. For higher CD effect, the analogue histidylalanine complex were used for CD measurements which were done by a Jasco J - 815 CD spectrometer.

3. Simulation of ESR spectra

Temperature dependent ESR spectra were simulated simultaneously by the EPRTEMP [2] program. The program fits the isotropic ESR parameters calculated for 273 K (g_o, A_o copper(II) hyperfine coupling, a_N nitrogen superhyperfine couplings) and the α, β, γ relaxation parameters which describe the linewidth ($W_{MI}=\alpha+\beta M_I+\gamma M_I^2$). The ESR parameters at a given temperature were calculated by the equation:

$$Q(T)=Q_o+Q_1(T-T_o)+Q_2(T-T_o)^2+Q_3(T-T_o)^3$$

where T_o= 273 K, Q_o is the value at 273 K and Q_1, Q_2, Q_3 coefficients can be fitted to describe the temperature dependence of Q(T). The isomer ratios were calculated by the Van't Hoff relation:

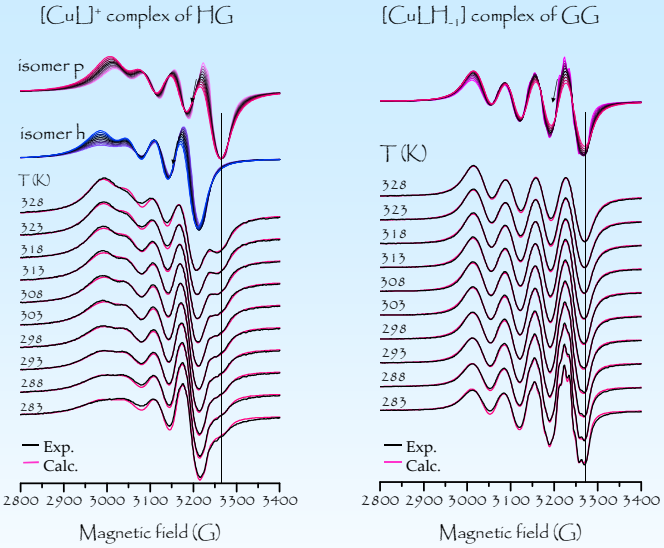
$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

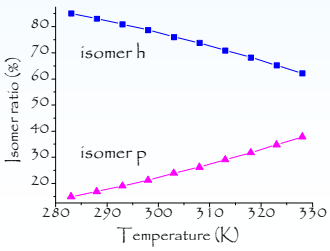
changing the thermodynamic parameters ΔH and ΔS.

2. A. Rockenbauer, N. V. Nagy, F. Le Moigne, et. al. *J. Phys. Chem. A* 2006, 110, 9542-9548

Isotropic ESR parameters at 273 K and their linear dependence by temperature.

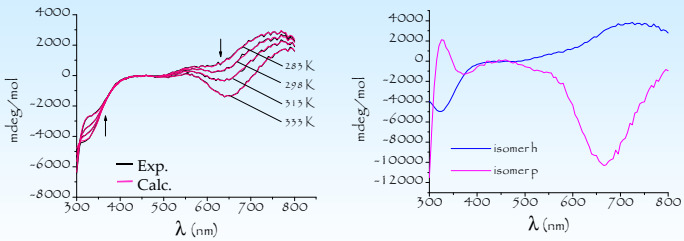
	L = HG				L = GG	
	isomer p		isomer h			
	Q_o	Q_1/deg	Q_o	Q_1/deg	Q_o	Q_1/deg
g_o	2,1153	1,2e-4	2,1437	6,8e-5	2,1202	-5,1e-4
A_o/G	63,0	0,036	60,4	-0,053	67,2	-0,007
a_{N1}/G	14,5	-	11,5	-	14,1	-
a_{N2}/G	14,0	-	12,5	-	11,7	-
α/G	21	0,235	34,1	-0,084	14,7	0,153
β/G	-9,8	0,055	-16,6	0,155	-6,7	0,072
γ/G	2.1	-	1,9	-	0,8	-





	ESR	CD
$\Delta H \left(\frac{kJ}{mol}\right)$	-21.36	-21.37
$\Delta S \left(\frac{J}{mol\,K}\right)$	-62.44	-60.90

4. CD measurements



Temperature dependent CD spectra could also be decomposed into two component curves. The alteration of the component ratios agrees well with ESR results.

5. Summary

Temperature dependent ESR and CD spectra offered detailed information about the peptide- and histamine-type coordination isomers of histidylglycine $[CuL]^+$ complex. The results showed unambiguously the existence of the two isomers, however, this detailed analysis resulted in the opposite isomer ratio compared to earlier results [1]. The histamine-type complex (~80 %) dominates at room temperature but its amount decrease rapidly with temperature and the percentage of the peptide-type complex at 55 °C could reach already 40 %. From the changes of the isomer ratio the thermodynamic parameters – the standard enthalpy and entropy changes – of the isomer equilibrium were also determined.

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