On the Structure of Poly-L-lysine-metal Complexes in Aqueous Solution

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Poly-L-lysine-copper(II) complex has been prepared as a model compound of a metalloenzyme and found to oxidize D-3,4-dihydroxyphenylalanine faster than L-enantiomorph at pH 10.5, where the polymer chain has helical structure to some extent.[1] It has been estimated that the cupric ion in the helical poly-L-lysine-copper(II) complex is coordinated by four amino nitrogens in the side chains of poly-L-lysine and, in addition, by a deprotonated nitrogen in the peptide bond of the polymer.[2]

We report herewith on the structures of the complexes prepared from poly-L-lysine and several metal salts, *i.e.*, nickel(II) nitrate, cobalt(II) nitrate, zinc(II) nitrate and potassium tetrachloropalladate(II). The pH titration and the measurements of circular dichroism (CD) and infrared absorption spectra were carried out for the polymer complexes formed in aqueous media.

The order of the stability constants of the complexes were estimated as $-\mathrm{Pd(II)} > -\mathrm{Cu(II)} > -\mathrm{Zn(II)} \approx -\mathrm{Ni(II)} \approx -\mathrm{Co(II)}$ from modified Bjerrum plots[3] of the pH titration data obtained for the solution, with a ratio 0.15 of molar concentration of the metal ion to residual molar concentration of poly-L-lysine C_M/C_R. The Bjerrum formation functions, $\bar{n}$'s, were found to approach *ca.* 4 for all the complexes examined, which shows that each metal ion is coordinated by four amino nitrogens.

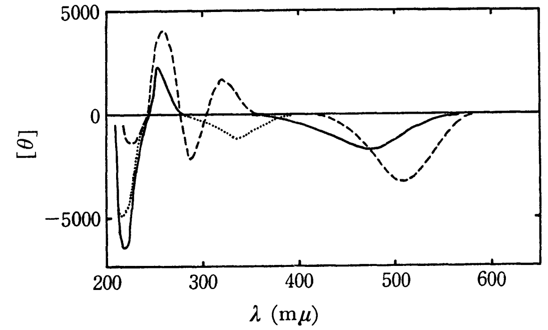

Fig. 1. CD spectra of poly-L-lysine-metal complexes (C_R= 0.005 M, C_M/C_R=0.15, pH 10.5); ---- Cu, —— Ni, ... Pd.

CD measurements were carried out at room temperature with a JASCO Model ORD/UV-5 optical rotatory dispersion recorder. The residual concentration of poly-L-lysine C_R and the ratio C_M/C_R were 0.005 mol/*l* and 0.15, respectively. All the polymer complexes showed n–π^* transition band due to helical structure at 222 mμ at pH 10.5. As in the case of poly-L-lysine-copper complex, only the poly-L-lysine-nickel and the poly-L-lysine-palladium complexes were found to show *d–d* transition and charge-transfer bands in addition to the band at 222 mμ (Fig. 1). The *d–d* transition bands are considered to be due to the vicinal effect of the asymmetric carbon of the poly-L-lysine through the coordination of the peptide group to the metal ion.

In order to ascertain the coordination of the peptide group in the cases of the nickel and the palladium complexes as done with the copper complex, the infrared absorption spectra in D_2O solutions at pD *ca.* 11 were recorded on a Hitachi Model EPI-G2 grating infrared spectrophotometer with small bags made of polyethylene film held between NaCl plates.[4] C_R and C_M/C_R were *ca.* 0.5 mol/*l* and 0.15, respectively. The amide I band of poly-L-lysine at pD *ca.* 11 shifts from 1640 cm^{-1} to 1610 cm^{-1} on the coordination of the peptide nitrogen to copper ion.[2] The band shifted to 1635 cm^{-1} and 1625 cm^{-1} for the nickel and the palladium complexes, respectively. No shift occurred in the case of the cobalt complex. The amide I band of glycylglycinate at 1632 cm^{-1} is known to shift to 1610 cm^{-1} and 1620 cm^{-1} when its deprotonated peptide nitrogen is coordinated to copper ion and nickel ion, respectively.[5] Thus the results seem to support the coordination of the peptide nitrogen to nickel and palladium ions as in the case of copper ion. They agree with those by CD measurement. In either of the nickel and the palladium complexes the metal ion seems to be coordinated by four amino nitrogens in the side chains of the helical poly-L-lysine and by a peptide nitrogen in the main chain of the polymer, which is similar to the case of poly-L-lysine-copper complex.

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